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Unexpected multiple coordination modes in silyl-bridged bis(phosphinine) complexes

Peter A. Cleaves^a and Stephen M. Mansell^{a*}

a: Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK.

*s.mansell@hw.ac.uk

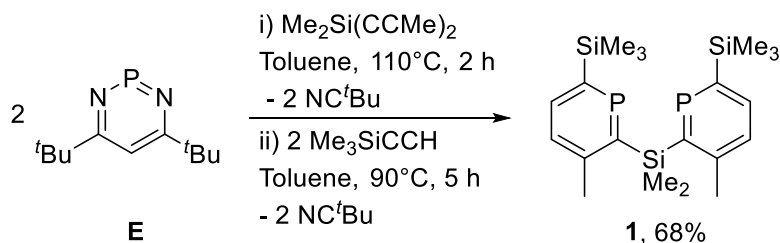
Abstract

The bis(phosphinine) [bis{3-methyl-6-(trimethylsilyl)phosphinine-2-yl}dimethylsilane] (**1**) was synthesised and its coordination chemistry explored. Molybdenum and chromium carbonyl complexes were crystallographically characterised featuring **1** bound η^6 through one phosphinine [$\text{Mo}(\text{CO})_3(\eta^6\text{-1})$] (**2Mo**), η^6 through both phosphinines to two metal centres [$\{\text{M}(\text{CO})_3\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-1})$] (**3M₂**, M = Cr, Mo) and chelating with η^1 coordination through both phosphines [$\text{M}(\text{CO})_4(\kappa\text{:}\eta^1\text{:}\eta^1\text{-1})$] (**4M**, M = Cr, Mo). However, only **3Mo₂** could be isolated analytically pure. Heating species **3Mo₂** in the presence of $[\text{Pd}(\text{COD})\text{Cl}_2]$ removed one CO ligand and generated [$\{\text{Mo}(\text{CO})_2\}(\mu\text{-}\kappa\text{:}\eta^1\eta^6\text{-}\eta^6\text{-1})\{\text{Mo}(\text{CO})_3\}$] (**5**), which is the first crystallised example of a bis(phosphinine) featuring chelating η^1 and η^6 coordination, as well as a metal centre bound to two phosphinines with different binding modes. In order to enforce a chelating bis- η^1 binding mode, the Ru complex [$\text{Ru}(\text{Cp}^*)(\text{Cl})(\kappa\text{:}\eta^1\text{:}\eta^1\text{-1})$] (**6**) was prepared demonstrating that judicious choice of metal fragment can dictate the coordination mode of a bis(phosphinine). Conversion of **6** to the hydride species [$\text{Ru}(\text{Cp}^*)(\text{H})(\kappa\text{:}\eta^1\text{:}\eta^1\text{-1})$] (**7**) afforded the first crystallographically characterised example of a complex with both phosphinine and hydride ligands at the same metal centre.

Introduction

Phosphinines (the phosphorus analogue of pyridine) are fascinating ligands in coordination chemistry because they contain phosphorus in an unusual, multiply-bonded environment.¹⁻⁶ This gives them unique properties including diagnostic $^{31}\text{P}\{^1\text{H}\}$ NMR resonances at high chemical shifts in an ‘aromatic’ region and variable binding modes such as η^6 -binding⁷⁻¹⁵ and non-directional η^1 -binding.¹⁶⁻¹⁸ Electronically, phosphinines function as π -accepting ligands³⁻⁵ but can also function as non-innocent ligands due to facile nucleophilic attack at P under certain conditions.¹⁹⁻²⁴ Monodentate phosphinine ligands²⁵⁻²⁹ and hybrid ligands,³⁰ where the phosphinine is connected to another donor,^{22-24, 26, 31-37} are

synthesised (Scheme 1) that facilitated the investigation of the coordination properties of a silyl-linked bis(phosphinine) and to make comparisons with the phosphine-aided bonding of **C**.

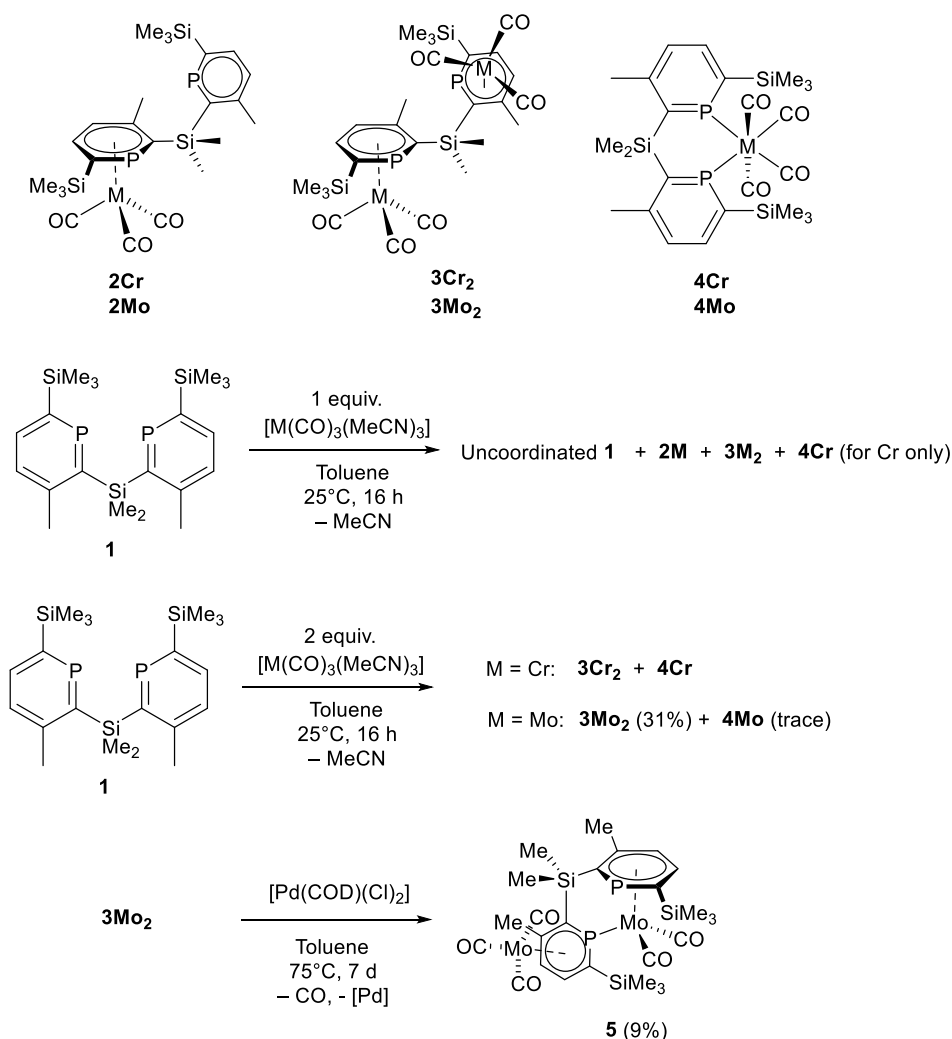


Scheme 1. Synthesis of bis(phosphinine) **1**.

Reaction of diazaphosphinine **E**^{44, 45} with dimethyldi(prop-1-ynyl)silane produced an intermediate bis(azaphosphinine) (³¹P{¹H} δ = 302.3 ppm) by a cycloaddition-cycloreversion mechanism, with concurrent loss of pivalonitrile-. A second cycloaddition-cycloreversion sequence using two equivalents of trimethylsilylacetylene afforded the bis(phosphinine) **1** with further loss of pivalonitrile. Following this conversion with ³¹P{¹H} NMR spectroscopy revealed an intermediate (azaphosphinine)(phosphinine) species, characterised by ³¹P{¹H} NMR spectroscopy as two doublets at δ = 302.0 and 261.6 ppm, and upon further reaction, the product was observed at δ = 260.9 ppm. Purification required column chromatography under N₂ because the product was sensitive to air. **1** was obtained in 68% yield and characterised by multinuclear NMR spectroscopy and mass spectrometry with an accurate mass for the correct formula determined.

Mono η^6 coordination

With **1** in hand, its coordination chemistry to group 6 metal carbonyl fragments was probed. Initially, we explored reactions with [M(CO)₄(NBD)] (M = Cr, Mo; NBD = norbornadiene), to which **C** had been successfully coordinated.⁵³ However, ³¹P{¹H} NMR spectroscopic studies revealed that no coordination took place at room temperature, and only after heating was a reaction seen. These precursors did not afford conversion to a single species cleanly, as prolonged heating of these mixtures showed evidence for decomposition as well as coordination, and alternative reagents were sought. Although the reaction of [Mo(CO)₃(η^6 -1,3,5-Me₃C₆H₃)] with **1** afforded many species, more success was achieved with [M(CO)₃(MeCN)₃] (M = Cr, Mo; Scheme 2).



Scheme 2. Preparation of Cr and Mo carbonyl complexes of **1**.

$[\text{M}(\text{CO})_3(\text{MeCN})_3]$ (M = Cr, Mo) complexes are very convenient sources of $\text{M}(\text{CO})_x$ fragments and the milder conditions helped to minimise the preparation of side products. Stirring a 1:1 mixture of $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ (M = Cr, Mo) with **1** at room temperature for 16 hours saw the formation of the mono η^6 -compounds **2M** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as a pair of doublets [M = Cr, $^{31}\text{P}\{^1\text{H}\}$ δ : 263.7, 65.1 ppm, $^4J_{\text{P-P}} = 17$ Hz; M = Mo, $^{31}\text{P}\{^1\text{H}\}$ δ : 264.0, 58.8 ppm, $^4J_{\text{P-P}} = 17$ Hz]. This splitting is indicative of two inequivalent phosphorus centres. As one of the doublets was at a very similar chemical shift to the free ligand ($^{31}\text{P}\{^1\text{H}\}$ δ ca. 264 ppm c.f. 261 ppm in **1**), it was assigned to a free, unbound phosphinine. The other resonance (δ ca. 60 ppm) corresponded to a phosphinine η^6 -bound to a metal centre. This is at higher frequency compared to some previous studies, which observed $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts for η^6 phosphinines between +41 and -20 ppm.⁷⁻¹³ Chemical shifts for several Rh η^6 -complexes are similar to those we observe (ca. 60 ppm), whereas Ir η^6 -complexes were at higher frequency (ca. 100 ppm).¹⁴ The bis(η^6 -phosphinine) species **3M₂** were also identified as singlet resonances by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (M = Cr, $\delta = 66.1$ ppm; M = Mo, $\delta = 59.4$ ppm), along with

unreacted ligand. Counter-intuitively, no NMR spectroscopic evidence for a Mo bis(η^1 -phosphinine) product was found.

All the volatiles were removed under reduced pressure to give red oils for both M = Cr and Mo. When M = Mo, storage of this oil as a solution in petroleum ether afforded red crystals of **2Mo** from the mixture with **3Mo₂**. Unfortunately, the corresponding chromium species **2Cr** could not be isolated as single crystals suitable for X-ray diffraction studies, and neither **2M** product could be isolated in a pure fashion. The molecular structure of **2Mo** (Figure 1) showed one phosphinine ring bound η^6 to a Mo(CO)₃ fragment, with the other uncoordinated. The η^6 -interaction showed a longer Mo-P bond distance (2.527(1) Å) than the Mo-C distances (2.411(4) - 2.327(5) Å). Coordination of the phosphinine ring has only marginally lengthened the bond lengths within the coordinated ring (P-C = 1.782(4) and 1.763(4), av. C-C = 1.416 Å) compared to the uncoordinated ring (P-C = 1.735(4) and 1.754(4), av. C-C = 1.394 Å). Two crystallographically characterised [Cr(CO)₃(η^6 -phosphinine)] complexes^{13, 15} and a [Cr(CO)₃(3-phosphaphenanthrene)] complex are known,¹¹ but no Mo(CO)₃ complexes have previously been described.

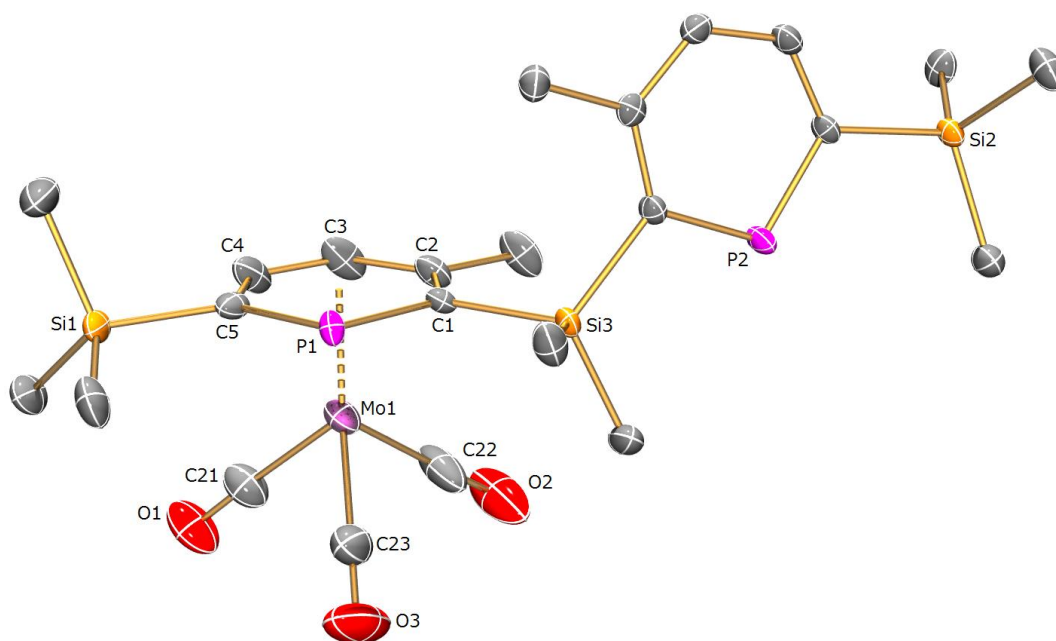


Figure 1. Molecular structure of **2Mo**, (thermal ellipsoids at 50% probability) with all H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)-P(1) 2.5269(11), Mo(1)-C_(phosphinine) range 2.327(5) – 2.411(4), Mo(1)-C_(CO) range 1.974(6) – 1.986(5), C(21)-O(1) – C(23)-O(3) range 1.147(6) – 1.148(6), C_(CO)-Mo(1)-C_(CO) range 83.6(2) – 88.4(2).

Synthesis of bis(η^6) and chelating bis(η^1) complexes

The selective preparation of the mono η^6 -phosphinine product was clearly hindered by the formation of multiple products, so the reaction with two equivalents of $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ was attempted. This worked successfully when $\text{M} = \text{Mo}$ as demonstrated by a singlet resonance at $\delta = 59.4$ ppm by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicative of bis(η^6 -coordination) in **3Mo₂**. This compound was isolated as an analytically pure compound in 31 % yield after recrystallisation and fully characterised by EA, multinuclear NMR spectroscopy and mass spectrometry. Interestingly, with the presence of planar-chirality in the coordination of $\text{Mo}(\text{CO})_3$ at either phosphinine ring, *rac* and *meso* diastereomers are possible, but the single $^{31}\text{P}\{^1\text{H}\}$ NMR singlet resonance indicates the presence of only one diastereomer. The *meso*-isomer of **3Mo₂** has time-averaged C_s symmetry in solution, which leads to the two phosphinine- $\text{Mo}(\text{CO})_3$ units being equivalent. However, the two Me groups on the SiMe_2 linker are not equivalent, and two different resonances are indeed observed by $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectroscopy for these two groups. For $\text{M} = \text{Cr}$, the reaction produced the analogous single diastereomer of **3Cr₂** ($\delta = 66.1$ ppm), along with the chelating bis(η^1 -phosphinine) complex **4Cr** ($\delta = 272.1$ ppm). Reaction of $[\text{Cr}(\text{CO})_3(\text{MeCN})_3]$ with **1** in a 3:1 ratio did not affect the resultant ratio of products, even after prolonged stirring. Thus, **3Mo₂** could be isolated as an analytically pure solid whereas **3Cr₂** and **4Cr** were always produced concurrently. Attempts to separate these complexes have not met with success, principally due to their very similar solubilities, which prevented their separation and precludes full characterisation. Attempts to purify using silica gel column-chromatography under a nitrogen atmosphere were unsuccessful, and these species decompose under air. Similar difficulties arose for the separation of **2M** and **3M₂**.

Single crystals of **3Cr₂** and **3Mo₂** were grown from saturated petroleum ether solutions. X-ray crystallographic analysis of **3Cr₂** (Figure S56) and **3Mo₂** (Figure 2) revealed very similar $[\{\text{M}(\text{CO})_3\}_2(\eta^6:\eta^6\text{-1})]$ complexes wherein both phosphinines are coordinated in an η^6 -fashion to separate $\text{M}(\text{CO})_3$ fragments. The *meso*-isomer was identified because M1 and M2 have opposite configurations, with the same true for M3 and M4 in the other molecule in the asymmetric unit. The M-P bond lengths in **3Mo₂** (av. 2.539 Å) are similar to that seen in **2Mo** but are longer than those in **3Cr₂** (av. 2.429 Å).

X-ray crystallographic experiments were performed on single crystals of **4Cr** grown from a saturated petroleum ether solution (Figure S57) and single crystals of **4Mo** (Figure 3) that were isolated in reactions of **1** with 2 equiv. $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ despite $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy not revealing an appreciable signal for this complex. The molecular structures of **4Cr** and **4Mo** were very similar with octahedral metal atoms, four CO ligands and *cis*-coordinated phosphinines. The plane defined by the

two phosphinine P atoms and the central Si atom (plane P(1)-P(2)-Si(3)) lies at an angle of 126.4 – 128.8° to the equatorial MP₂C₂ plane demonstrating that the bis(phosphinine) is not coplanar to the equatorial plane due to a steric clash between the equatorial CO ligands and the SiMe₃ substituents. However, the Mo-P bond lengths (2.470(1) and 2.478(1) Å) are shorter than that seen in **D**: [Mo(CO)₄(C)] (2.5028(4) Å).⁵³ The Cr-P bond lengths in **4Cr** are 2.327(2) and 2.330(2) Å, which are shorter than that observed in [Cr(CO)₄(C)] (2.3752(5) Å).⁵³

Upon re-analysis of the spectra collected for heated reactions of **1** with [Mo(CO)₄(NBD)] and [Mo(CO)₃(MesH)], we can now postulate that one of the products, observed at 280.4 ppm, is likely to be **4Mo**, and this value is in agreement with the value of 272.1 ppm attributed to **4Cr**.

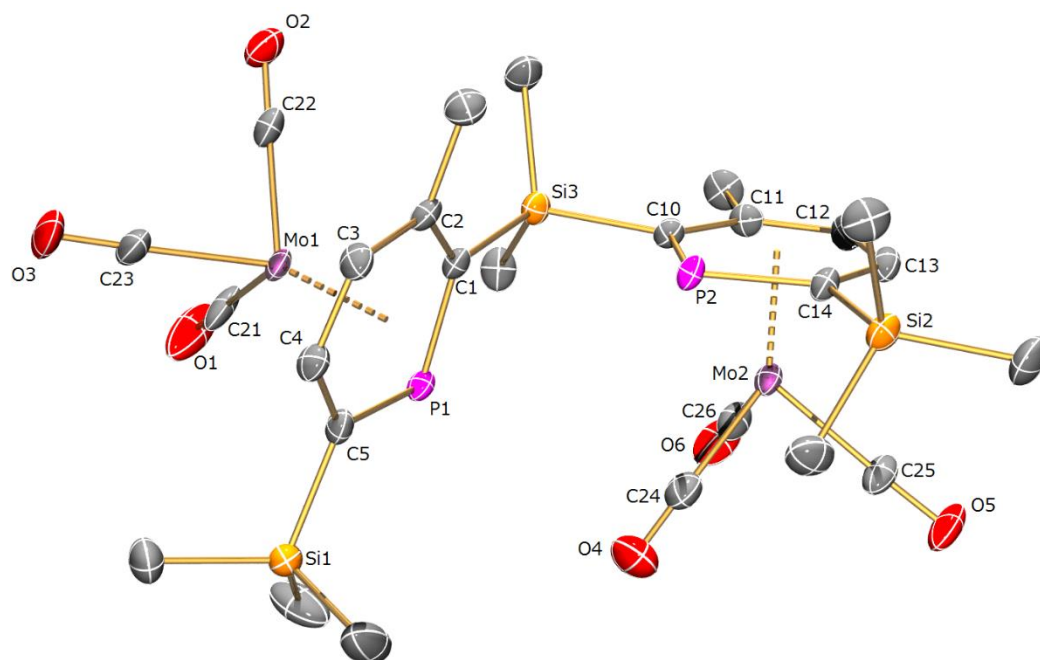


Figure 2. Molecular structure of **3Mo₂**, (thermal ellipsoids at 50% probability) with all H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)-P(1) 2.5422(11), Mo(1)-C_(phosphinine) range 2.323(4) – 2.419(4), Mo(1)-C_(CO) range 1.979(5) – 1.995(5), C(21)-O(1) – C(23)-O(3) range 1.153(6) – 1.160(6), Mo(2)-P(2) 2.5348(11), Mo(2)-C_(phosphinine) range 2.329(4) – 2.408(4), Mo(2)-C_(CO) range 1.993(5) – 2.003(5), C(24)-O(4) – C(26)-O(6) range 1.146(6) – 1.152(6), C_(CO)-Mo(1)-C_(CO) range 86.2(2) – 87.7(2), C_(CO)-Mo(2)-C_(CO) range 86.9(2) – 89.21(19).

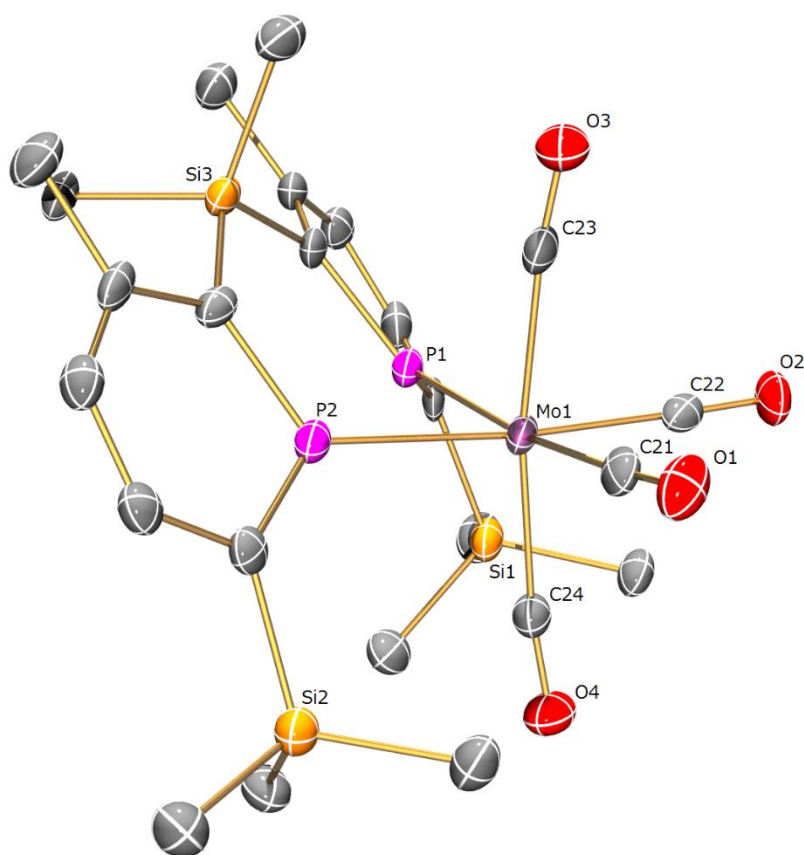


Figure 3. Molecular structure of **4Mo**, (thermal ellipsoids at 50% probability) with all H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)-P(1) 2.4697(10), Mo(1)-P(2) 2.4777(10), Mo(1)-C_(CO) range 1.993(4) – 2.051(4), C(21)-O(1) – C(24)-O(4) range 1.139(4) – 1.149(4), P(1)-Mo(1)-P(2) 85.39(3), P-Mo(1)-C_(cis) range 85.79(11) – 98.38(11), C-Mo(1)-C_(cis) range 83.61(15) – 89.98(15), C(23)-Mo(1)-C(24)_(trans) 171.35(14).

Chelating $\eta^6:\eta^1$ coordination

We then investigated whether it was possible to observe both η^6 and η^1 binding modes in a single complex. In the literature, there exist several examples of two metal fragments being coordinated to one phosphinine.⁵⁴⁻⁵⁸ To explore the possibility of a heterometallic species of **1**, wherein the phosphinines are chelating in a bis η^1 fashion to one metal centre whilst maintaining η^6 coordination to Mo(CO)₃ fragments, we reacted **3Mo**₂ with either [Ru(Cp*)(Cl)]₄ or [Pd(COD)(Cl)]₂. Heating these mixtures in C₆D₆ afforded red solutions with other insoluble by-products, but ³¹P{¹H} NMR spectroscopy revealed that only the red solutions contained ³¹P NMR resonances. Comparison of the ³¹P{¹H} NMR spectroscopic data from both these reactions revealed a pair of doublets (J = 3.5 Hz) at 150.9 and 34.5 ppm, suggesting that the same product results from both reactions, and therefore

must only contain molybdenum. This transformation was only complete for the reaction with [Pd(COD)(Cl)₂], with residual **3Mo₂** observed for [{Ru(Cp*)(Cl)}₄]. The chemical shift of these phosphorus peaks suggest that one phosphinine has remained in an η^6 coordination (34.5 ppm), as the resonance is only slightly shifted from that observed in **3Mo₂**, and towards the region previously identified for η^6 coordination as outlined above. The other resonance (150.9 ppm) occurs in a region as yet not observed for these phosphinine species, and suggests some alternative coordination mode.

Scale up of the reaction with [Pd(COD)(Cl)₂] in toluene afforded, after 7 days heating at 75 °C, a red solution with insoluble by-products.⁵⁹ Removal of volatiles *in vacuo*, and extraction into petroleum ether, followed by storage of this saturated solution at -28 °C afforded the product as dark red crystals in low yield (**5**, 9%). Analysis by X-ray crystallographic studies revealed **5** to contain two differing Mo centres (Figure 4). Mo(1) features a piano stool geometry with three carbonyl ligands and η^6 coordination to a phosphinine ring (P(1), C(1)-C(5)), as observed in the starting material **3Mo₂**. This phosphinine is simultaneously interacting with the Mo(2) in an η^1 manner. The second phosphinine is only bound η^6 to Mo(2), which completes its coordination sphere with two carbonyl ligands. The η^1 interaction in **5** between Mo(2) and P(1) is 2.5895(6) Å, which is longer than the comparable distances in **4Mo** (2.4697(10) – 2.4777(10) Å). The bond distances between Mo and atoms in the η^6 coordinated phosphinines remain unchanged from the precursor **3Mo₂**.

To the best of our knowledge, complex **5** is the first crystallographically characterised example of: i) a bis(phosphinine) where one phosphinine (here the heterocycle incorporating P(1)) is coordinated in both an η^1 and an η^6 fashion, ii) a bis(phosphinine) chelating a metal through η^6 and η^1 binding, and iii) a metal centre (here Mo(2)) bound to two phosphinine units with different binding modes. Complex **5** thus demonstrates a combination of interesting coordination motifs for phosphinines previously undescribed for a bis(phosphinine).

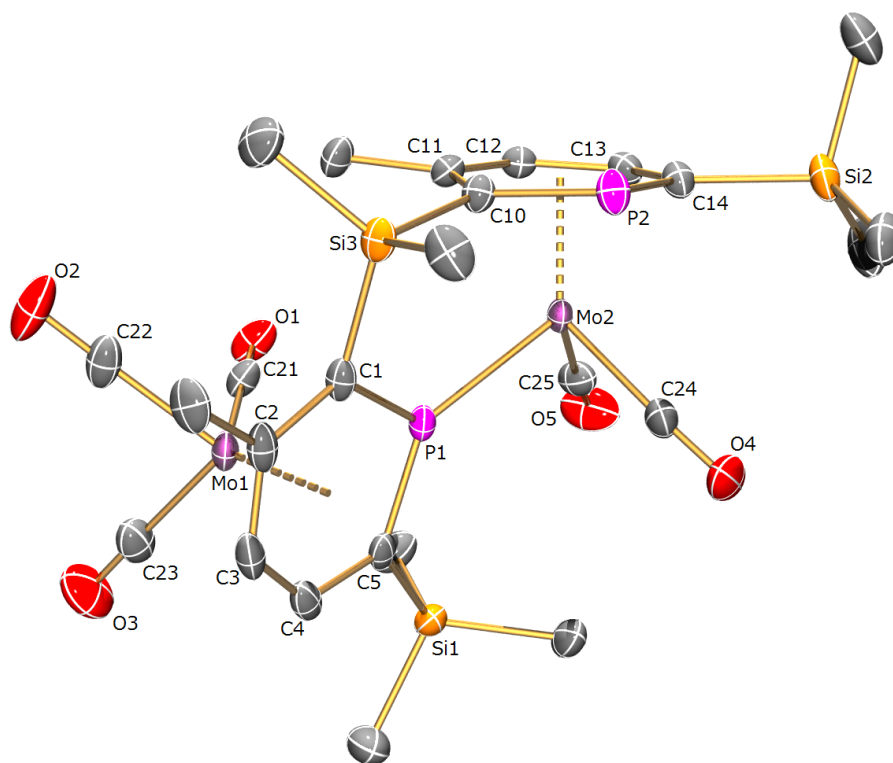


Figure 4. Molecular structure of **5**, (thermal ellipsoids at 50% probability) with all H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)-P(1) 2.5895(6), Mo(1)-C_(phosphinine) range 2.326(2) – 2.419(2), Mo(1)-C_(CO) range 1.973(3) – 1.980(3), C(21)-O(1) – C(23)-O(3) range 1.149(3) – 1.151(3), Mo(2)-P(1) 2.3748(6), Mo(2)-P(2) 2.5404(7), Mo(2)-C_(phosphinine) range 2.306(2) – 2.393(2), Mo(2)-C_(CO) range 1.970(3) – 1.977(3), C(24)-O(4) – C(26)-O(6) range 1.154(3) – 1.160(3), C_(CO)-Mo(1)-C_(CO) range 84.76(12) – 89.42(12), Mo(2)-P(1)-C(3) 165.15(6), P(1)-Mo(2)-C(24) 89.60(8), P(1)-Mo(2)-C(25) 97.17(8), C(24)-Mo(2)-C(25) 85.26(12).

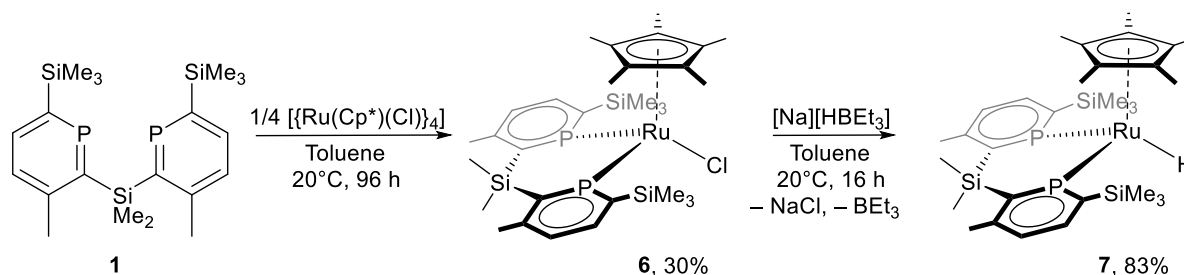
Attempted ethylene oligomerisation catalysis

Coordination chemistry with M(CO)_x fragments has thus revealed a greatly increased preference for η^6 -coordination compared to phosphinophosphinine **C**. Ligand **C** was previously found to be an interesting ligand for the Cr-catalysed oligomerisation of ethylene, producing the commercially important alpha olefins 1-hexene and 1-octene, as well as unusual alkene and alkane products with a cyclopentane ring.⁵³ In order to probe whether the differences in coordination chemistry observed for **1** had an impact on this reaction, we repeated the standard conditions for Cr-catalysed ethylene oligomerisation that were used for ligand **C**, namely in-situ catalyst generation using [Cr(acac)₃], the ligand and MMAO in chlorobenzene under 40 bar(g) ethylene. We found that with **1**, no reaction of the ethylene was observed, and no alpha olefins or polymer was observed. This is in contrast to

reactions of $[\text{Cr}(\text{acac})_3]/\text{MMAO}$ without a phosphorus-based ligand which mainly produces polymer.⁵³ From this we infer that ligand **1** has coordinated to the Cr ions (which are stripped of the acac ligands by the MMAO) in order to suppress the ligand-free reactivity. Although the geometry of the complex is not known, η^6 -phosphinine coordination would be in general agreement with literature observations that η^6 -arene coordination is not conducive to catalysis.⁶⁰⁻⁶⁵

[RuCp*] coordination and reactivity

Given that the coordination mode for **1** is variable in group six metal carbonyl chemistry, we were interested in exploring how bis(η^1 -coordination) can be enforced. Our previous work with phosphinophosphinines^{20, 21} led us to choose the [RuCp*] fragment (Scheme 3).



Scheme 3. Preparation of **6** and **7**.

Stirring a 1:4 mixture of $\{\{\text{RuCp}^*(\text{Cl})\}_4\}:\mathbf{1}$ in toluene cleanly generated a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 272.5 ppm, reminiscent of the chemical shifts for **4M**, and in agreement with the desired bidentate phosphinine complex, $[\text{Ru}(\text{Cp}^*)(\text{Cl})(\eta^1:\eta^1\text{-}\mathbf{1})]$, **6**. Removal of volatiles *in vacuo*, followed by extraction of the resultant red solid into petroleum ether afforded, upon storage for 16 h, red crystals that were revealed to be **6**. Further extraction of the solid into toluene afforded crystals of **6**•toluene (Figure 4).

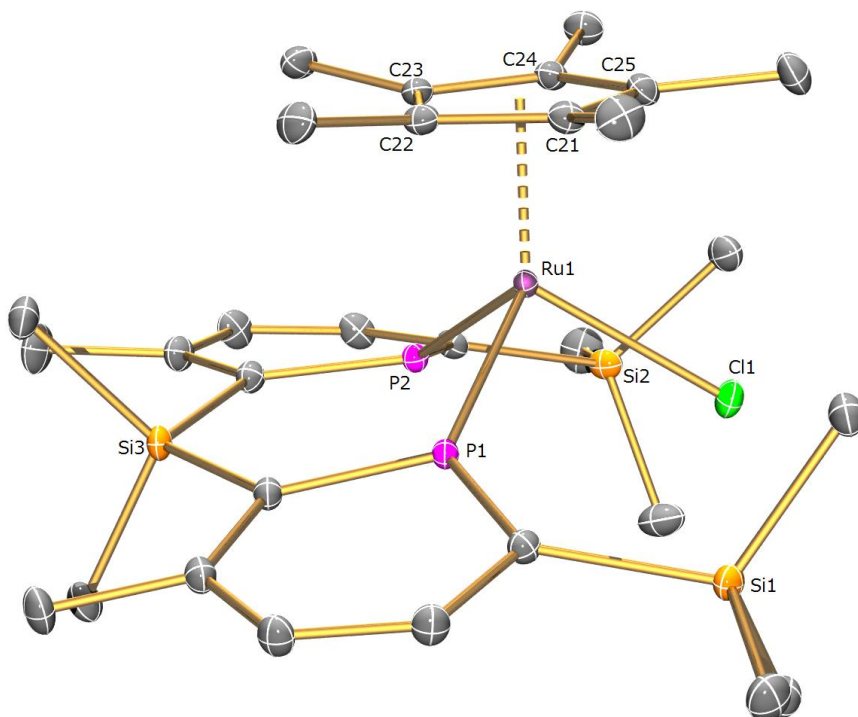


Figure 5. Molecular structure of **6**•toluene, (thermal ellipsoids at 50% probability) with all H atoms and lattice solvent (toluene) omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)-P(1) 2.2600(3), Ru(1)-P(2) 2.2530(4), Ru(1)-C_(cp*) range 2.2090(13) – 2.2655(13), Ru(1)-Cl(1) 2.4308(4), P(1)-Ru(1)-P(2) 92.519(13), P(1)-Ru(1)-Cl(1) 94.920(12), P(2)-Ru(1)-Cl(1) 94.935(13).

X-ray crystallographic analyses of **6** revealed bidentate η^1 coordination of the bis(phosphinine) ligand to a Ru centre with a “piano stool” type geometry, where the coordination sphere completed by the chloride ligand and Cp*. As in **4M**, the ligand in **6** is distorted away from the plane Ru(1)-P(1)---P(2), (angle with the plane P(1)-P(2)-Si(3) 135.291 – 137.240°) such that it is nearly coplanar to the plane through the Cp* ligand (plane C(21)-C(23)-C(24), 3.689 – 5.062°). This contrasts to the coordination of the bis(phosphinine) tmbp ligand in [Ru(Cp*)(Cl)(**A**)], where the ligand and the Ru(1)--P(1)--P(2) plane are nearly coplanar.⁶⁶ The Ru-P bond lengths (2.2530(4) and 2.2600(3) Å) are shorter than that seen in **4M** (2.470(1) and 2.478(1) Å), but slightly longer than those in the **A** analogue (2.2375(7) and 2.2475(7) Å).⁶⁶

The substitution of the chloride for a hydride ligand was attempted because there are no crystallographically characterised complexes containing a phosphinine and a hydride ligand. These species are of interest because ruthenium-hydride species are implicated as intermediates in studies of ruthenium catalysed transfer hydrogenation and hydrogen borrowing processes.²⁰ To this end, we reacted **6** with [Na][HBEt₃] in toluene. The solution darkened, and upon removal of volatiles *in vacuo*

afforded a dark oil. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed a new signal at 286.3 ppm which became a doublet upon removing the ^1H decoupling ($^2J = 37$ Hz), assignable to $[\text{Ru}(\text{Cp}^*)(\text{H})(\eta^1:\eta^1\text{-1})]$, **7**. Furthermore, the ^1H NMR spectrum revealed a triplet resonance at -10.4 ppm, typical of Ru-H chemical shifts,⁶⁷ and indicative of a hydride coupling to two equivalent phosphinine centres. Extraction into petroleum ether and filtering, followed by further extraction into $\text{Me}_3\text{SiOSiMe}_3$ afforded yellow crystals. Single crystals suitable for single crystal X-ray diffraction were grown from the benzene and revealed that the product was indeed the ruthenium hydride complex, **7**.

The bis(phosphinine) ligands in **7** are coordinated *cis* in an η^1 fashion to a “piano stool” ruthenium centre. As in **6**, **7** demonstrates the non-linearity of the phosphinine ligand, though to a lesser degree (plane P(1)-P(2)-Si(3) to plane Ru(1)-P(1)-P(2) 131.436°), and the co-planarity between the phosphinine and the Cp* ring is also lessened (plane P(1)-P(2)-Si(3) to plane C(21)-C(23)-C(24) 10.344°). To the best of our knowledge, complex **7** represents the first example of a TM complex with both phosphinine and hydride ligands.

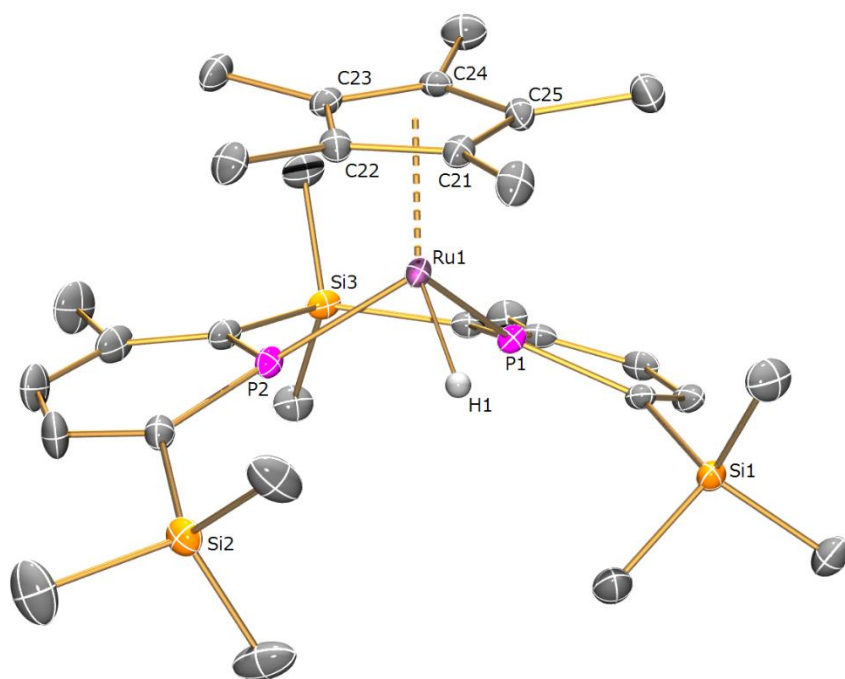


Figure 6. Molecular structure of **7**, protons omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Ru(1)-P(1) 2.2046(6), Ru(1)-P(2) 2.1992(6), Ru(1)-C(Cp^*) range 2.257(2) – 2.286(2), Ru(1)-H(1) 1.58(3), P(1)-Ru(1)-P(2) 89.60(2), P(1)-Ru(1)-H(1) 85.7(10), P(2)-Ru(1)-H(1) 89.9(9).

Conclusions

In conclusion, we have prepared a series of mono and bis- η^6 phosphinine complexes (**2M**, **3M₂**, M = Cr, Mo), and bis(η^1 -complexes) (**4M**, M = Cr, Mo) coordinated to group six carbonyl fragments. Only **3Mo₂** can be isolated as a pure compound due to competition between the binding modes. By adapting the metal precursor, we can direct the coordination environment towards bis- η^1 , as observed for the ruthenium species **6** and **7**. Whilst the conversion of **3Mo₂** to **5Mo** demonstrates that there is some scope to alter the coordination environment of metal carbonyl species and generate η^1 -binding, a more practical solution to enforce controlled binding at a metal centre requires careful selection of metal fragments, with [Ru(Cp*)(Cl)] proving to be very useful. The coordination of the bis(phosphinine) **1**, which can vary between these common binding modes, is therefore in direct contrast to more rigid ligand structures, such as the bis(phosphinine) **A**, or phosphinophosphinine **C**. The synthesis of the first example of a complex containing phosphinine and hydride ligands at the same metal centre clearly indicates that under the right conditions, these complexes can be stable with respect to nucleophilic attack of the phosphinine P atom.

EXPERIMENTAL

All reactions were performed under an oxygen-free (H_2O , $\text{O}_2 < 0.5$ ppm) nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNIlab Plus glovebox. Anhydrous toluene was obtained from an MBRAUN SPS-800 and 40-60 petroleum ether was distilled from sodium wire; benzene and benzene-d₆ were dried over molten potassium and distilled. All anhydrous solvents were degassed before use and stored over activated molecular sieves.

The following compounds were prepared according to literature methods: 4,6-di-tert-butyl-1,3,2-diazaphosphinine,⁴⁴ dimethyldi(prop-1-ynyl)silane,⁶⁸ [Mo(CO)₃(MeCN)₃],⁶⁹ [Mo(CO)₄(NBD)] (NBD = norbornadiene, C₇H₈),⁷⁰ [Mo(CO)₃(MesH)] (MesH = mesitylene, 1,3,5-Me₃C₆H₃),⁷¹ [Cr(CO)₃(MeCN)₃],⁷² [Cr(CO)₄(NBD)],⁷⁰ [Ru(Cp*)(Cl)]₄ (Cp* = C₅Me₅),⁷³ [Pd(COD)(Cl)₂] (COD = 1,4-cyclooctadiene).⁷⁴ The following were purchased from commercial suppliers and used without further purification: Me₂SiCl₂, BrMgC≡CMe, HC≡CSiMe₃, NaHBET₃ (1 M in THF), [Pd(Cl)₂] and cyclooctadiene.

Air sensitive samples for NMR spectroscopy were prepared in NMR tubes equipped with a J. Young tap. NMR spectra were recorded on Bruker AVI400 (400 MHz) or AVIII400 (400 MHz) spectrometers at 25 °C unless specified. Chemical shifts δ are noted in parts per million (ppm). ¹H and ¹³C spectra were calibrated to the residual proton resonances of the deuterated solvent. ²⁹Si and ³¹P NMR spectra were referenced to external samples of SiMe₄ and 85% H₃PO₄, respectively, as 0 ppm. X-ray diffraction

experiments were performed on single crystals of the samples covered in inert oil and placed under the cold stream (100 K) of a Bruker X8 APEXII four-circle diffractometer (Heriot-Watt University), except for **5**, which was collected in the cold stream (120 K) of an Oxford Diffraction four-circle Supernova diffractometer (University of Edinburgh). Exposures were collected using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Indexing, data collection and absorption corrections were performed, and structures were solved using direct methods (SHELXT) and refined by full-matrix least-squares (SHELXL) interfaced with the programme OLEX2. CCDC deposition numbers: 1892336 – 1892344 Elemental analyses were performed by Dr Brian Hutton at Heriot-Watt University using an Exeter CE440 elemental analyser or by Mr Stephen Boyer at London Metropolitan University. Mass spectrometry analysis was performed at the EPSRC UK National Mass Spectrometry Facility at Swansea University, using an Atmospheric Solids Analysis Probe interfaced to a Water Xevo G2-S instrument. FTIR was performed on a Thermo Scientific Nicolet iS5/iD5 ATR spectrometer.

Preparation [2-{3-Me-6-(SiMe₃)-1-PC₅H₂}₂SiMe₂], (**1**)

To a solution of 4,6-di-tert-butyl-1,3,2-diazaphosphinine [3,5-^tBu-PN₂C₃H], (**E**, 19.50 mmol) in toluene (60 mL), prepared *in situ* according to literature precedent,⁴⁴ in a Young's tapped 250 mL ampoule, was added Me₂Si(C \equiv CMe)₂ (1.018 g, 7.48 mmol). The solution was heated to 110 °C for 2 h. An aliquot of the resultant mixture was analysed in C₆D₆ by ³¹P{¹H} NMR spectroscopy, and additional Me₂Si(C \equiv CMe)₂ (0.310 g, 2.28 mmol) was added to ensure the correct stoichiometry, and the mixture heated to 110 °C for 2 h, to effect total conversion to the bis(azaphosphinine)dimethylsilane intermediate. Trimethylsilylacetylene (2 mL, 14.43 mmol) was added and the mixture was heated at 90 °C for 5 h. An aliquot of the resultant mixture was analysed in C₆D₆ by ³¹P{¹H} NMR spectroscopy, and more HC \equiv CSiMe₃ (1.18 mL, 8.52 mmol) was added, and the mixture heated to 110 °C for 5 h, to effect total conversion to bis(phosphinine)dimethylsilane (**1**). Purification was achieved by air-free column chromatography with degassed hexanes, to afford a colourless oil, which solidifies at ambient temperature. Unfortunately, crystals suitable for X-ray diffraction studies could not be isolated. Yield: 2.769 g, 68%.

³¹P{¹H} NMR (C₆D₆, 298 K): $\delta = 260.9$ ppm (s). ¹H NMR (C₆D₆, 298 K): $\delta = 7.87$ (multiplet, 2H, Ar-H (*meta* to P)), 6.94 (d, ³J_{HH} = 8.07 Hz, 2H, Ar-H (*para* to P)), 2.26 (s, 6H, Ar-Me), 0.98 (t, ⁴J_{HP} = 2.08 Hz, 6H, SiMe₂), 0.37 ppm (s, 18H, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 298 K): $\delta = 139.04$ (s, Ar), 138.98 (s, Ar), 138.93 (s, Ar), 130.15 (s, Ar), 129.89 (s, Ar), 138.93 (s, Ar), 26.51 (s, CH₃), 1.56 (t, J = 13.20 Hz, Si(CH₃)₂), 1.02 ppm (s, Si(CH₃)₃). ²⁹Si{¹H} NMR (C₆D₆, 298 K): $\delta = -2.08$ (d, ²J_{SIP} = 36.19 Hz, SiMe₃), -7.88 ppm (t, ²J_{SIP} = 38.15 Hz, SiMe₂). HRMS (ASAP/TOF) *m/z*: Calcd. for C₂₀H₃₄P₂Si₃: 420.1444; Found 420.1443. FTIR

ν/cm^{-1} (ATR): 2953 (m), 1512 (m), 1442 (w), 1403 (w), 1360 (m), 1264 (s), 1247 (s), 1158 (w), 1032 (m), 912 (s), 829 (s), 798 (s), 767 (s), 750 (s), 718 (m), 690 (m), 673 (s), 633 (s).

Preparation of $[\text{Cr}(\text{CO})_4(\kappa:\eta^1:\eta^1-1)]$, (**4Cr**) and $[\{\text{Cr}(\text{CO})_3\}_2(\mu-\eta^6:\eta^6-1)]$, (**3Cr₂**)

To $[\text{Cr}(\text{CO})_3(\text{MeCN})_3]$ (0.271 g, 1.05 mmol) was added toluene (15 mL) and a solution of **1** in toluene (0.223 g in 5 mL, 0.53 mmol) at room temperature. The orange suspension was stirred at room temperature for 96 h, to afford a red solution. Volatiles were removed *in vacuo* to afford an orange oil, and the product was extracted with pet. ether (15 mL). The volume of this red solution was reduced to 4 mL, and storage at -28°C for 7 days afforded red crystals of **4Cr**. Continued storage of this solution (without filtration) at -28°C for 14 days afforded a further batch of crystals, which were identified as **3Cr₂**. Collection of this mixed sample by filtration afforded a crystalline mass of 138 mg.

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 272.1 (s, **4Cr**), 66.1 ppm (s, **3Cr₂**).

Preparation of $[\{\text{Mo}(\text{CO})_3\}_2(\mu-\eta^6:\eta^6-1)]$, (**3Mo₂**)

To a mixture of **1** (0.526 g, 1.25 mmol) and $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ (108 mg, 0.36 mmol) was added toluene (5 mL) at room temperature. The resultant suspension was stirred at room temperature for 16 h. An aliquot of the red solution produced was analysed in C_6D_6 by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Volatiles were removed *in vacuo*, and more $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ was added to the resultant red solid. This process of addition of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ was repeated until the solution remained cloudy (total Mo reagent added, 0.816 g, 2.688 mmol), and the $^{31}\text{P}\{^1\text{H}\}$ NMR showed the presence of only one species. The suspension was filtered to afford a brown solid (devoid of signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum) and a red solution. Volatiles were removed *in vacuo*, and the red sticky solid was extracted with pet. ether (10 mL). This solution was concentrated to ca. 5 mL, and red crystals of **3** were formed on storage of this solution at 5°C for 16 h (0.307 g, 0.393 mmol, 31%).

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 59.4 ppm (s). ^1H NMR (C_6D_6 , 298 K): δ = 5.52 (multiplet, 2H, Ar-H (*meta* to P)), 4.66 (d, $^3J_{\text{HH}}$ = 6.85 Hz, 2H, Ar-H (*para* to P)), 2.07 (s, 6H, Ar-Me), 0.70 (t, $^4J_{\text{HP}}$ = 2.69 Hz, 3H, SiMe₂), 0.39 (s, 3H, SiMe₂), 0.07 ppm (s, 18H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 218.96 (s, CO), 121.37 (s, Ar-Me), 105.35 (m, Ar), 104.31 (m, Ar), 104.30 (s, Ar-H), 88.51 (m, Ar-H), 26.11 (t, J = 2.97 Hz, Me), 5.74 (t, $^3J_{\text{CP}}$ = 14.12 Hz, SiMe), 5.26 (t, $^3J_{\text{CP}}$ = 5.20 Hz, SiMe), 0.35 ppm (d, $^3J_{\text{CP}}$ = 2.97 Hz, SiMe₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 1.91 (d, $^2J_{\text{SiP}}$ = 35.21 Hz, SiMe₃), -1.53 ppm (t, J = 32.28 Hz, SiMe₂). Anal. calcd for $\text{C}_{26}\text{H}_{34}\text{Mo}_2\text{O}_6\text{P}_2\text{Si}_3$: C 40.0; H 4.39; N 0. Found C 39.93; H 4.46; N 0. HRMS (ASAP/TOF) m/z :

(**3Mo₂-CO+H**) Calcd. for C₂₅H₃₅⁹²Mo₂O₅P₂Si₃: 744.9404; Found 744.9406. FTIR ν/cm^{-1} (ATR): 2959 (w), 1972 (s), 1912 (s), 1888 (s), 1447 (w), 1407 (w), 1378 (w), 1337 (w), 1251 (m), 1089 (m), 1030 (m), 909 (s), 832 (s), 800 (s), 768 (m), 753 (m), 694 (m), 666 (m).

Preparation of [**Mo(CO)₃{Mo(CO)₂{ μ - η^6 - κ^2 : η^1 : η^6 -1}**], (**5**)

To a mixture of **3Mo₂** (0.156 g, 0.20 mmol) and [Pd(COD)(Cl)₂] (0.057 g, 0.20 mmol) was added toluene (5 mL) at room temperature. The resultant suspension was heated at 75 °C for 7 d, until all **3Mo₂** had been consumed (as confirmed by ³¹P{¹H} NMR spectroscopy). Volatiles were removed *in vacuo* to afford a brown solid, which was extracted into pet. ether (15 mL). The resultant red solution was concentrated to 2 mL, and storage of this solution at -28 °C for 3 d afforded dark red crystals of **5Mo**. Crystalline yield 14 mg, 9%.

³¹P{¹H} NMR: δ 150.9 (d, ⁴J_{PP} = 3.47 Hz, η^6 : η^1 -phosphinine), 34.5 ppm (d, ⁴J_{PP} = 3.47 Hz, η^6 -phosphinine). ¹H NMR (C₆D₆, 298 K): δ = 5.55 (dd, 1H, *J* = 20.05 Hz, *J* = 6.85 Hz, Ar-*H*), 5.05 (m, 2H, Ar-*H*), 4.31 (d, 1H, *J* = 6.85 Hz, Ar-*H*), 2.18 (s, 3H, Ar-*Me*), 1.75 (s, 3H, Ar-*Me*), 0.41 (s, 9H, SiMe₃), 0.35 (s, 3H, SiMe), 0.30 (s, 9H, SiMe₃), 0.21 ppm (s, 3H, SiMe). ¹³C{¹H} NMR (C₆D₆, 298 K): δ = 221.30 (2C, CO), 218.95 (3C, CO), 119.77 (d, 1C, *J* = 5.94 Hz, Ar), 118.46 (d, 1C, *J* = 7.43 Hz, Ar), 105.08 (t, 1C, *J* = 8.92 Hz, Ar), 93.79 (m, 2C, Ar), 91.54 (d, 1C, *J* = 8.92 Hz, Ar), 85.27 (d, 1C, *J* = 16.35 Hz, Ar), 25.87 (s, 1C, Ar-*Me*), 23.07 (d, 1C, *J* = 5.95 Hz, SiMe), 22.37 (s, 1C, Ar-*Me*), 1.01 (s, 3C, SiMe₃), 0.79 (s, 3C, SiMe₃), -0.64 ppm (d, 1C, *J* = 5.94 Hz, SiMe). Several Ar carbons were not observed by ¹³C NMR, probably due to low intensity and coupling to ³¹P{¹H}. ²⁹Si{¹H} NMR (C₆D₆, 298 K): δ = 3.83 (d, SiMe₃, ²J_{SiP} = 21.52 Hz), 2.80 (SiMe₃, ²J_{SiP} = 29.34 Hz), 0.54 ppm (t, SiMe₂, ²J_{SiP} = 31.30 Hz). Anal. calcd for C₂₅H₃₄Mo₂O₅P₂Si₃•0.25(C₅H₁₂): C 40.91; H 4.84; N 0. Found C 40.53; H 5.28; N 0. HRMS (ASAP/TOF) *m/z*: (**5+H**) C₂₅H₃₅⁹²Mo₂O₅P₂Si₃: 744.9404; Found 744.9417. FTIR ν/cm^{-1} (ATR): 2952 (m), 2864 (m), 1973 (m), 1935 (m), 1896 (m), 1597 (m), 1578 (m), 1553 (w), 1528 (m), 1489 (w), 1461 (w), 1425 (w), 1387 (m), 1360 (m), 1315 (m), 1272 (w), 1248 (m), 1196 (m), 1179 (m), 1135 (w), 1066 (s), 1028 (w), 908 (s), 873 (w), 837 (m), 814 (w), 781 (w), 749 (m).

Preparation of [**Ru(Cp*)(Cl)(κ : η^1 : η^1 -1)**], (**6**)

To [**Ru(Cp*)(Cl)₄**] (0.084 g, 0.077 mmol) was added toluene (15 mL) and a solution of **1** in toluene (0.130 g in 3 mL, 0.31 mmol) at room temperature. The red brown suspension was stirred at room temperature for 96 h, to afford a red solution. Volatiles were removed *in vacuo* to afford a red solid. Extraction of this solid with pet. ether (20 mL), concentration of the resultant red solution to 5 mL,

and storage at $-28\text{ }^{\circ}\text{C}$ for 16 h afforded red crystals of **6** (47 mg, 0.068 mmol, 22%). Further extraction of the crude solid with 10 mL toluene, and storage of this solution at $-28\text{ }^{\circ}\text{C}$ for 16 h afforded red crystals of **6**•toluene (19.2 mg, 0.024 mmol, 8%).

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 272.5 ppm (s). ^1H NMR (C_6D_6 , 298 K): δ = 7.99 (m, 2H, Ar-H (*meta* to P)), 6.80 (d, $^4J_{\text{HP}}$ = 8.31 Hz, 2H, Ar-H (*para* to P)), 2.28 (s, 6H, Ar-Me), 1.31 (t, J = 2.69 Hz, 15H, Cp*), 0.78 (s, 3H, SiMe), 0.73 (s, 18H, SiMe₃), 0.18 ppm (s, 6H, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 158.46 (s, Ar), 150.78 (s, Ar), 144.18 (t, $^3J_{\text{CP}}$ = 9.66 Hz, Ar-H), 138.61 (s, Ar), 126.72 (t, $^2J_{\text{CP}}$ = 18.58 Hz, Ar-H), 91.92 (s, Cp), 26.24 (s, Ar-Me), 10.64 (s, CpMe₅), 7.72 (s, SiMe), 7.38 (s, SiMe) 4.01 ppm (s, SiMe₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 1.79 (t, J = 9.78 Hz, SiMe₂), -9.91 ppm (t, $^2J_{\text{SiP}}$ = 19.56 Hz, SiMe₃). Anal. calcd for $\text{C}_{30}\text{H}_{49}\text{ClP}_2\text{RuSi}_3\cdot 0.2(\text{C}_5\text{H}_{12})$: C 52.67; H 7.33; N 0. Found C 52.54; H 7.54; N 0. HRMS (ASAP/TOF) m/z : (**6**-Cl) Calcd. for $\text{C}_{30}\text{H}_{49}\text{P}_2^{96}\text{RuSi}_3$: 657.1668; Found 657.1680. FTIR ν/cm^{-1} (ATR): 2960 (w), 2903 (w), 1512 (w), 1451 (w), 1407 (w), 1354 (w), 1259 (s), 1239 (m), 1217 (w), 1151 (w), 1086 (m), 1017 (s), 944 (w), 923 (s), 836 (s), 797 (s), 760 (s), 748 (m), 716 (m), 697 (m), 639 (m).

Preparation of $[\text{Ru}(\text{Cp}^*)(\text{H})(\kappa\text{:}\eta^1\text{:}\eta^1\text{-1})]$, (**7**)

To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of **6** (88.8 mg, 0.128 mmol) in toluene (10 mL) was added $[\text{NaHBEt}_3]$ (0.13 mL, 1 M in THF). The resultant mixture was warmed to room temperature and stirred for 2 hours. An aliquot was taken and analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, revealing incomplete conversion to a new product. The solution was cooled, and a further 0.1 mL of $[\text{NaHBEt}_3]$ was added. The resultant mixture was allowed to return to room temperature with stirring for 16 h. Volatiles were removed *in vacuo* to afford a black oil, which was extracted with 8 mL pet. ether to give a dark red solution and a pale solid (~5 mg). Volatiles were again removed *in vacuo* and the resultant solid extracted into $\text{Me}_3\text{SiOSiMe}_3$ (5 mL). This red solution was reduced *in vacuo* to afford a yellow crystalline solid. Crystalline yield: 70 mg, 83%.

$^{31}\text{P}\{^1\text{H}\}$ NMR: δ 286.2 ppm (s). ^{31}P NMR: δ 286.3 ppm (d, $^4J_{\text{PP}}$ = 37.65 Hz). ^1H NMR (C_6D_6 , 298 K): δ = 7.72 (m, 2H, Ar-H (*meta* to P)), 6.74 (d, 2H, $^3J_{\text{HH}}$ = 7.70 Hz, Ar-H (*para* to P)), 2.34 (s, 6H, Ar-Me), 1.71 (s, 15H, C₅Me₅) 0.92 (s, 3H, SiMe), 0.58 (s, 18H, SiMe₃), 0.33 (s, 3H, SiMe), -10.36 ppm (t, 1H, $^2J_{\text{HP}}$ = 37.23 Hz, Ru-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 155.69 (s, Ar), 151.15 (s, Ar), 142.82 (t, $^3J_{\text{CP}}$ = 8.17 Hz, Ar-H), 129.03 (s, Ar-Me), 124.85 (t, $^2P_{\text{CP}}$ = 17.83 Hz, Ar-H), 94.00 (s, 5C, Cp), 26.52 (s, Ar-Me), 11.57 (s, C₅Me₅), 7.30 (s, SiMe), 5.29 (s, SiMe), 1.76 ppm (s, SiMe₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = -1.73 (s, SiMe₃), -9.72 ppm (t, $^2J_{\text{SiP}}$ = 19.56 Hz, SiMe₂). Anal. calcd for $\text{C}_{30}\text{H}_{50}\text{P}_2\text{RuSi}_3$: C 54.76; H 7.66; N 0. Found C 54.55; H 7.86; N 0. HRMS (ASAP/TOF) m/z : (**7**+H) Calcd. for $\text{C}_{30}\text{H}_{49}\text{P}_2^{96}\text{RuSi}_3$: 653.1844; Found 653.1831. FTIR

ν/cm^{-1} (ATR): 2961 (w), 2901 (w), 1954 (w), 1506 (w), 1446 (w), 1404 (w), 1374 (w), 1351 (w), 1259 (m), 1213 (w), 1153 (w), 1085 (m), 1016 (s), 950 (w), 928 (m), 834 (s), 793 (s), 753 (s), 717 (m), 688 (m), 638 (m), 599 (m), 572 (s).

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:10.1021/xxx. Spectroscopic data for **1 – 7** and additional crystallographic information. (PDF)

Notes

The authors declare no competing financial interest.

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