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Editorial

# Synergy between Main Group and Transition Metal Chemistry

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Since the pioneering studies of Alfred Werner at the beginning of the 20th Century [1], the interplay between ligands, primarily derived from the p-block of the main group elements, and transition metals has been shown to be of vital importance in inorganic chemistry (Figure 1). For instance, the series of compounds  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (violet),  $\text{CoCl}_3 \cdot 4\text{NH}_3$  (green),  $\text{CoCl}_3 \cdot 5\text{NH}_3$  (purple), and  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (yellow) came to be understood in terms of an octahedral Co(III) centre with different coordination environments: *cis*- and *trans*- $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ ,  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ , and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , respectively [2].

A more sophisticated understanding of the synergy between ligands, transition metal reactivity, and applications in homogeneous catalysis, initially focused on phosphine complexes, was developed by Chadwick Tolman at DuPont's Central Research and Development Department in the 1960s and 1970s [3]. Since then, the concept of synergy in inorganic chemistry has bloomed, with key areas of research including mixed-metal bases focused on s-block metals that have shown enhanced reactivity and selectivity [4], and the concept of metal-ligand cooperativity, where ligands play an active role in the key bond-breaking and bond-making steps in catalysis [5].

This Special Issue on *Synergy Between Main Group and Transition Metal Chemistry* demonstrates the breadth of modern research in inorganic chemistry. The organometallic chemistry of Rh complexes featuring unusual [N,O] bidentate ligands was studied by Elmakki, Venter, Roodt, and co-workers, with a focus on the oxidative addition of MeI, demonstrating the power of spectroscopic techniques in deducing the fate and mechanism of the reaction of different Rh centres, particularly in a bimetallic complex [6]. [N,O] ligands were also used in new Sn(II) chemistry, described by Johnson and co-workers based on deprotonated 2-hydroxypyridine. The importance of the structure of the ligand and its impact on the aggregation state was demonstrated, particularly when comparing the results to ligands with an extended distance between the N and O donors, providing a series that contained 4-, 5-, and 6-membered chelate rings [7]. Further studies on the coordination of the Sn atom are also possible, thereby expanding the exciting coordination chemistry and reactivity of transition metal stannylene complexes. Similarly, the Ge cations described by Reid and co-workers showed the expanding coordination chemistry of main group compounds, an area that is underexplored compared to transition metal analogues [8]. The coordination chemistry of chloranilate with niobium described by Belay, Venter, Roodt, and co-workers also demonstrated the interplay of the coordination environment and the aggregation of metal centres [9].



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s block		Transition Metals										Main Group					
1												p block					
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H Hydrogen	He Helium											B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine	Ne Neon
Li Lithium	Be Beryllium											Al Aluminum	Si Silicon	P Phosphorus	S Sulfur	Cl Chlorine	Ar Argon
Na Sodium	Mg Magnesium	Sc Scandium	Ti Titanium	V Vanadium	Cr Chromium	Mn Manganese	Fe Iron	Co Cobalt	Ni Nickel	Cu Copper	Zn Zinc	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium	Br Bromine	Kr Krypton
K Potassium	Ca Calcium	Y Yttrium	Zr Zirconium	Nb Niobium	Mo Molybdenum	Tc Technetium	Ru Ruthenium	Rh Rhodium	Pd Palladium	Ag Silver	Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium	I Iodine	Xe Xenon
Rb Rubidium	Sr Strontium	* Lanthanoids	Hf Hafnium	Ta Tantalum	W Tungsten	Re Rhenium	Os Osmium	Ir Iridium	Pt Platinum	Au Gold	Hg Mercury	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium	At Astatine	Rn Radon
Cs Cesium	Ba Barium	** Actinoids	Rf Rutherfordium	Db Dubnium	Sg Seaborgium	Bh Bohrium	Hs Hassium	Mt Meitnerium	Ds Darmstadtium	Rg Roentgenium	Cn Copernicium	Nh Nihonium	Fl Flerovium	Mc Moscovium	Lv Livermorium	Ts Tennessine	Og Oganesson
Fr Francium	Ra Radium																

  

f block																
*	**	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
		La Lanthanum	Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
		Ac Actinium	Th Thorium	Pa Protactinium	U Uranium	Np Neptunium	Pu Plutonium	Am Americium	Cm Curium	Bk Berkelium	Cf Californium	Es Einsteinium	Fm Fermium	Md Mendelevium	No Nobelium	Lr Lawrencium

**Figure 1.** Divisions within the periodic table of elements. Figure adapted from work by Dr M. Haddow (University of Edinburgh), with permission.

The coordination chemistry of alane ( $\text{AlH}_3$ ) with carbenes was explored in detail by Weetman and co-workers. Interestingly, they utilised the percent buried volume—an extension of Tolman's ideas on quantifying the steric bulk—to quantify the size taken up by the carbene ligand bound to aluminium, reporting alane fragments bound to the largest and smallest NHCs reported to date [10]. Ligands containing group 13 elements are of increasing importance thanks to their use and generation in homogeneous catalysis, such as transition metal-catalysed C–H borylation. Liptrot and co-workers took a different approach by investigating the frustrated Lewis pair concept as applied to an NHC complex of copper(I) boryliminomethanide. A range of reactivity was observed, demonstrating that many pathways are possible when ligands become more than spectators to metal-centered reactivity [11]. Finally, coinage metal complexes—in this case, gold—of unconventional group 15 ligands were described by Mansell and co-workers. For a bis(phosphinine), a stable digold complex was generated, whereas a phosphinophosphinine complex readily decomposed, thus reinforcing the presence of additional pathways when ligands become directly involved in chemistry [12]. Overall, we hope that this Special Issue draws increasing attention to the interplay between main group elements and transition metals, whether there are direct bonds, subtleties introduced to the coordination chemistry, or new reaction pathways that are now available, and we hope that this Issue will keep interest in this field high.

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