Dimetalla-Heterocyclic Carbenes: The Interconversion of Chalcocarbonyl and Carbido Ligands

Harrison J. Barnett and Anthony F. Hill*

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The μ -carbido complexes $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ and $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{dppm})_2]$ cleave CS_2 to afford the monothiocarbonyl complexes $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ and $[\text{Rh}_2(\mu\text{-CS})\text{Cl}_2(\text{dppm})_2]$. The latter reacts with dimethyl acetylenedicarboxylate (DMAD) to afford $[\text{Rh}(\mu\text{-CS})(\mu\text{-DMAD})\text{Cl}_2(\text{dppm})_2]$. This complex is also formed from $[\text{Rh}(\mu\text{-C})(\mu\text{-DMAD})\text{Cl}_2(\text{dppm})_2]$ and sulfur. These strategies also afford the first rhodium selenocarbonyl complexes $[\text{Rh}(\mu\text{-CSe})\text{Cl}_2(\text{dppm})_2]$ and $[\text{Rh}(\mu\text{-CSe})(\mu\text{-DMAD})\text{Cl}_2(\text{dppm})_2]$.

Binuclear μ -carbido complexes present four distinct bonding scenarios (Chart 1) reflecting the effective atomic number requirements (1-3 valence electrons) of the metal termini.¹⁻⁴

Chart 1. Distinct Bimetallic μ -Carbido Bonding Modes.¹⁻⁴

Whilst an understanding of the bonding within bimetallic carbidos is emerging^{1n,3g,4a,4b} their reactivity remains essentially uncharted. Reactivity studies are limited to various co-ligand substitutions,^{1l,1m,2b,2g,3e,4a} oxidation to a CO ligand (Class A),^{1l} protonation to afford a μ -methyldiyne (Class B^{2b} or D^{4b}), CS_2 -insertion (Class B),^{2b} halogenation to afford μ -halocarbynes (Class A)^{1m} and interconversion of bonding classes (Classes C $\rightarrow$ B^{3e,f} and A $\rightarrow$ D^{4a}). For Class D μ -carbidos, the bent geometry at carbon renders it nucleophilic in reactions with various electrophiles (CO_2 , MeOH, chalcogens, metals).⁴

The Class A complex $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ (**1**) is readily accessible *via* the reaction of $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ (**2**) with catecholborane^{1l} however the mechanism of its formation, remains obscure. Attempts to extend this desulfurisation to numerous other rhodium thiocarbonyl complexes or $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ have yet to find success. To generally explore

the reactivity of bridging carbido ligands and, more specifically, processes that involving carbon-chalcogen bond cleavage^{1d,k,o,2e} or formation,^{4b} we now discuss the reactions of dirhodium carbido complexes with CS_2 and chalcogens.

Documented reactions of metal-carbon multiple bonded species with CS_2 are somewhat scarce,⁵ being limited to the inferred intermediacy of a thiocarbonyl-carbyne complex *en route* to a thioketenyl;^{5a} and the cleavage of CS_2 by the carbyne complexes $[\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Mo}(\equiv\text{CR})(\text{CO})(\text{L})(\text{Tp})]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me}-4$; $\text{L} = \text{CO}$, PPh_3 ; $\text{Tp} = \text{hydrotris}(\text{pyrazolyl})\text{borate}$) to afford the thiobenzoyl complex $[\text{Ru}(\eta^2\text{-SCPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ ^{5b} or the thioketene complex $[\text{Mo}(\kappa^2\text{-}\eta^2,\sigma'\text{-SCRCOS})(=\text{O})(\text{Tp})]$, respectively.^{5c} For carbene complexes, Young has described a thioketene pincer complex arising from the reaction of an alkylidene pincer with CS_2 and PPh_3 ,^{5d} while Bourissou has observed the insertion of CS_2 into a gold(III) carbene complex.^{5e}

Treating complex **1** with CS_2 at room temperature results in spectroscopically quantitative formation to two equivalents of the thiocarbonyl complex $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ ⁶ (**2**, Scheme 1, CDCl_3 : $\delta_{\text{P}} = 31.0$, $^1J_{\text{RhP}} = 142$ Hz). There is no indication of the formation of Ph_3PS ($\delta_{\text{P}} \approx 35$) confirming that the carbido ligand serves as the sulfur abstracting agent for coordinated CS_2 . In contrast, treating **1** with elemental sulfur leads to complex degradation and formation of Ph_3PS , without any observable **2** being formed. Given that the reaction is accompanied by complete rupture of the $\text{Rh}=\text{C}=\text{Rh}$ spine, the reaction of the dppm-bridged bimetallic complex $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\mu\text{-dppm})_2]$ (**3**, dppm = bis(diphenylphosphino)methane),^{1m} with CS_2 was investigated. In general, two bridging dppm ligands confer considerable stability on bimetallic 'A-frame' assemblies.⁷

Surprisingly, the product of this reaction was the coordinatively unsaturated *mono*-thiocarbonyl complex $[\text{Rh}_2(\mu\text{-CS})\text{Cl}_2(\mu\text{-dppm})_2]$ (**4**, Figure S1), which could also be spectroscopically observed to form when **3** was treated with

^a Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia. Email: a.hill@anu.edu.au
Electronic CCDC 2013308 - 2013311 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Scheme 1. Reactions of μ -carbido complexes with CS_2 and chalcogens (R = CO_2Me ; i = CS_2 , ii = $\text{HBO}_2\text{C}_6\text{H}_4$, iii = $1/8 \text{ S}_8$, iv = $1/n \text{ Se}_n$, v = $\text{RC}\equiv\text{CR}$).

elemental sulfur but *not* with methylthiirane (*vide infra*) nor when $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ was treated with dppm . The corresponding carbonyl analogue of **4** is well known⁸ and the structural features of interest pertaining to the $\text{Rh}_2(\mu\text{-CA})$ (A = O,^{8c} S) core are essentially comparable (Table S1). The Rh–Rh bond length (2.7059(4) Å) is very marginally contracted upon replacing oxygen by sulfur, while the Rh–C bond lengths are, within precision limits, similar for both complexes. The bonding within the Rh_2CS unit is consistent with a canonical depiction involving Rh–C and Rh–Rh single bonds on the basis of experimentally determined mean bond lengths (1.915(6) and 2.7121(6) Å). These are not dissimilar to those calculated (DFT: $\omega\text{B97X-D}/6\text{-31G}^*/\text{LANL2DZ}$, 1.930 and 2.727 Å see ESI) for the hypothetical model complex $[\text{Rh}_2(\mu\text{-CS})\text{Cl}_2(\mu\text{-dppm})_2]$ (dppm = bis(dimethylphosphino)methane) which has Löwdin bond orders of 1.12 (Rh–C) and 0.77 (Rh–Rh) and associated natural charges of +0.48 (Rh), –0.55 (C) and –0.05 (S). The HOMO (See ESI Figure S10) comprises both $\text{Rh}(d_{z^2})$ orbitals and sulfur lone pair character (alternative sites for electrophilic attack), while the HOMO-1 and HOMO-4 orbitals contribute primarily to Rh–C and Rh–Rh σ -bonding respectively.

For the reactions of both **1** and **3** we envisage initial coordination of CS_2 to one of the coordinatively unsaturated rhodium centres (**E**, Scheme 1)⁹ followed by a cyclo-addition with one $\text{Rh}=\text{C}$ multiple bond *via* a hetero-alkene metathesis mechanism (**F**, Scheme 1).^{5b,10} Ring cleavage of the metallacyclic thione then generates two new thiocarbonyl ligands on adjacent metals. For the reaction involving **3**, a similar cleavage would be expected to generate the unknown bimetallic species $[\text{Rh}_2\text{Cl}_2(\text{CS})_2(\text{dppm})_2]$ (*cf.* the known dicarbonyl analogue⁸), from which dissociation of CS is required to provide **4**. Notably, in

contrast to CO it is extremely rare for thiocarbonyl ligands to simply dissociate,¹¹ given the high energy of free CS.

The complex **3** also slowly reacts with elemental selenium to form the a μ_2 -selenocarbonyl complex $[\text{Rh}_2(\mu\text{-CSe})\text{Cl}_2(\mu\text{-dppm})_2]$ (**5**, Figure 1). Selenocarbonyl complexes remain rare¹¹ and group 9 examples are limited to an *isoselenocarbonyl* complex^{12a} and those derived from $[\text{IrCl}(\text{CSe})(\text{PPh}_3)_2]$.^{12b} The C=Se bond length of 1.747(8) Å is significantly shorter than the imprecise bond lengths ($R_1 = 0.094$) in the only other known symmetrically bridging^{11e} CSe complex $[\text{Ru}_2(\mu\text{-CSe})(\mu\text{-NPh})(\eta\text{-C}_5\text{Me}_5)_2]$ (1.802(13), 1.844(12) Å).^{4b} Replacement of sulfur in **4** by selenium in **5** results in a significant (106 e.s.d.) elongation of the Rh–Rh bond (mean 2.7754(9) Å *cf.* 2.7121(6) in **4**). This elongation is not computationally replicated for the model complexes $[\text{Rh}_2(\mu\text{-CA})\text{Cl}_2(\text{dmpm})_2]$ (A = O, S, Se; see ESI) indicating the involvement of packing effects.

Figure 1. Molecular structure **5** in a crystal of **5**.(PhMe)_{1.5} (50% displacement ellipsoids, solvent and hydrogen atoms omitted, dppm groups simplified, one of two crystallographically molecules shown, See Table S1, ESI). Selected bond lengths (Å) and angles (°): Rh1–Rh2 2.7577(8), Rh1–Cl1 2.351(2), Rh1–C1 1.911(9), Rh2–C1 1.928(8), Se1–C1 1.747(8), C1–Rh1–Rh2 43.8(3), Rh2–C1–Rh1 91.8(4), Se1–C1–Rh1 134.0(6). Insets: alternative views along and orthogonal to the Rh_2C plane.

The reactions of terminal carbido complexes with chalcogens have been shown to afford chalcocarbonyl ligands^{2d,11e,13} and the formulation of a putative unstable Class **D** carbido has also been substantiated by its conversion to the corresponding thio- are selenocarbonyl derivatives.^{4b} The isolable Class **D** carbido $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\mu\text{-DMAD})(\mu\text{-dppm})_2]$ (**6**, DMAD = dimethyl acetylenedicarboxylate)^{4a} displays a bent (Rh–C–Rh = 124.7°) carbido ligand, the nucleophilicity of which is manifest in reactions that append slender metal halides such as AuCl and CuCl. The reaction of **6** with elemental sulfur at room temperature primarily affords the thiocarbonyl complex $[\text{Rh}_2(\mu\text{-CS})\text{Cl}_2(\mu\text{-DMAD})(\mu\text{-dppm})_2]$ (**7**) in moderate yields that were compromised by some degradation of the A-frame architecture. Surprisingly, use of the typically milder single atom sulfur transfer reagent methylthiirane¹⁴ led to complete destruction of the complex such that dppm-S and dppm-S_2 were the predominant phosphorus-containing products observed (³¹P NMR). An alternative synthesis of **7** was achieved *via* the facile addition of DMAD to **3** (Scheme 1). All spectroscopic data associated with **7** indicate that it is C_{2v} -symmetric in solution, however attempts to grow crystals resulted in the isolation of the mono-*aquo* complex $[\text{Rh}_2(\mu\text{-CS})\text{Cl}_2(\text{OH}_2)(\mu\text{-DMAD})(\mu\text{-$

dppm)₂] (**7a**, Figure 2). Similar behaviour was encountered for the trigonal carbido complexes [Rh₂M(μ₃-C)Cl₃(OH₂)(μ-DMAD)(μ-dppm)₂] (M = Cu, Au) such that while the water molecule does not remain bound in solution, the symmetry reduction (C_{2v}→C_s) upon coordination of water to a *single* rhodium impacts upon crystallisation.

Figure 2. Molecular structure **7a** in a crystal of **7a**·CHCl₃ (50% displacement ellipsoids, most hydrogen atoms omitted, dppm and ester groups simplified). Selected bond lengths (Å) and angles (°): Rh1–Cl1 2.4741(12), Rh1–O1 2.300(4), Rh1–C2 2.020(4), Rh1–C1 1.935(5), Rh2–C1 1.954(5), Rh2–C3 2.000(5), S1–C1 1.625(5), C2–C3 1.350(7), Rh1–C1–Rh2 122.0(2), S1–C1–Rh1 130.3(3), S1–C1–Rh2 107.8(2). Inset shows view orthogonal to the Rh₂C plane.

Prior to the advent of **4** and **7a**, structural data for homobimetallic μ-thiocarbonyl ligands were somewhat sparse¹⁵ with none available for rhodium. Far more geometric data for bridging chalcocarbonyls have however emerged from extensive computational studies by King and Li.¹⁶ Symmetrical μ-CS coordination is expected to weaken the CS multiple bond and the CS bond lengths found for **4** (1.619(4) Å) and **7a** (1.625(5) Å) fall towards the long end of the somewhat large range (1.575^{15a} to 1.629 Å^{4b}). The Rh–C(S) bond lengths primarily reflect the increase in rhodium coordination number proceeding from **4** (1.914(4) Å) to the five (1.954(5) Å) and six coordinate (1.935(5) Å) rhodium centres in **7a**.

Class **D** bent carbido complexes might be considered to in some respects mimic isolobal *N*-heterocyclic carbenes (NHC), not least in their ability to coordinate to extraneous metal centres.⁴ To quantify the donor properties of the increasing diversity of NHC ligands, Ganter has proposed employing the ⁷⁷Se NMR shift of the corresponding selenone.¹⁷ The “carbene” **6** also reacts slowly with selenium (but not tellurium) to afford *inter alia* [Rh₂(μ-CSe)Cl₂(μ-DMAD)(μ-dppm)₂] (**8**, 14%). Whilst the yield is disappointing, **5** and **8** are nevertheless the first rhodium selenocarbonyl complexes and **8** could also be formed in an identical manner to **7** through addition of DMAD to **5**. As with **7**, the complex crystallises with a water molecule coordinated to *one* rhodium centre, *viz.* [Rh₂(μ-CSe)(OH₂)Cl₂(μ-DMAD)(μ-dppm)₂] (**8a**, Figure 3). Recent developments in selenocarbonyl and tellurocarbonyl chemistry have identified a diversity of bridging coordination modes,^{11e,18} though **5** and **8a** are two of only three complexes^{4b} to display the symmetrical bridging mode. The ν_{CSe} infrared absorption is tentatively assigned to a band of medium intensity at 1000 cm⁻¹ (*cf.* 957 cm⁻¹

¹ for **5**), that is absent in the precursor and based on Redlich-Teller considerations correlates with those found at 1249 cm⁻¹ for **7** and 1700 cm⁻¹ for [Rh₂(μ-CO)Cl₂(μ-DMAD)(μ-dppm)₂].^{8b} In the infrared spectra of terminal selenocarbonyls, the ν_{CSe} mode is typically the most intense, however for **5** and **8** these modes are weak, as could be computationally substantiated for the model complexes [Rh₂(μ-CSe)Cl₂L_n] (L_n = dmpm, dHpm, (CO)₄, (CO)₆) and [Rh₂(μ-CSe)(μ-HCCH)Cl₂(dmpm)₂] (ν_{CSe} : 970–1030 cm⁻¹; see ESI Table S1). The C1–Se1 bond length (1.785(6) Å) is longer than in **4** but still within the range found for terminal CSe complexes (1.608–1.786 Å)^{11,18} and shorter than found in NHC-derived selenones (1.82–1.84 Å),¹⁷ or selenoureas, *e.g.*, 1.844(4) Å for (Me₂N)₂C=Se.¹⁹

Figure 3. Molecular structures of **8a** in a crystal of **8a**·(PhMe)(CH₂Cl₂)_{0.5}, (50% displacement ellipsoids, solvents and hydrogen atoms omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): Rh2–Se1 2.8947(8), Rh2–C1 1.935(6), Rh2–C3 2.008(6), Rh1–Cl1 2.4783(15), Rh1–O1 2.289(5), Rh1–C1 1.927(6), Rh1–C2 2.017(6), Se1–C1 1.785(6), Rh1–C1–Rh2 124.2(3), Se1–C1–Rh2 102.1(3), Se1–C1–Rh1 133.6(3). Inset Rh₂CSe plane of **8a** (blue) superimposed on that of the precursor **6** (red).

Turning to Ganter’s ⁷⁷Se NMR derived parameters, we might anticipate that the ⁷⁷Se NMR spectrum of **8** comprises a single 15-line (tripled pentet, ¹⁰³Rh and ³¹P: *I* = ½) resonance at *ca* δ_{Se} = 530 ppm based on the HOMO-LUMO gap for **6**. Unfortunately, scanning the complete ~3000 ppm range for known selenium shifts failed (as with δ_C) to identify a signal even employing a 133.4 MHz instrument, due to the high order coupling to ¹⁰³Rh and ³¹P (see ESI).

In conclusion, whilst CS₂ has proven to be a valuable source molecule for the installation of μ-carbido ligands in bimetallic complexes,^{1d,1h,1n} it is now found to be capable of undergoing coupling reactions with established carbido ligands to ultimately (re)generate thiocarbonyls. The addition of chalcogens to a Class **D** μ-carbido complex has allowed the construction of CS and CSe complexes further reinforcing the Class **D**/NHC analogy to provide the first rhodium selenocarbonyls.

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