View Article Online

# ChemComm

Chemical Communications

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Hill and H. J. Barnett, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC05106C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

# **Chemical Communications**

# COMMUNICATION

# DOI: 10:1059/D0CC05106

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

Harrison J. Barnett and Anthony F. Hill\*

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 04 September 2020. Downloaded on 9/6/2020 6:59:22 AM

The  $\mu$ -carbido complexes  $[Rh_2(\mu-C)Cl_2(PPh_3)_4]$  and  $[Rh_2(\mu-C)Cl_2(dppm)_2]$  cleave  $CS_2$  to afford the monothiocarbonyl complexes  $[RhCl(CS)(PPh_3)_2]$  and  $[Rh_2(\mu-CS)Cl_2(dppm)_2]$ . The latter reacts with dimethyl acetylenedicarboxylate (DMAD) to afford  $[Rh(\mu-CS)(\mu-DMAD)Cl_2(dppm)_2]$ . This complex is also formed from  $[Rh(\mu-C)(\mu-DMAD)Cl_2(dppm)_2]$  and sulfur. These strategies also afford the first rhodium selenocarbonyl complexes  $[Rh(\mu-CSe)Cl_2(dppm)_2]$  and  $[Rh(\mu-CSe)(L_2(dppm)_2]$ .

Binuclear  $\mu$ -carbido complexes present four distinct bonding scenarios (Chart 1) reflecting the effective atomic number requirements (1-3 valence electrons) of the metal termini.<sup>1-4</sup>

L <sub>n</sub> M=c=ML <sub>n</sub>	L <sub>n</sub> M <b>≡c</b> —ML <sub>n</sub>	L <sub>n</sub> M <b>≡c</b> :→ML <sub>n</sub>	
Class <b>A</b> Dimetallacumulene	Class <b>B</b> Metallacarbyne	Class <b>C</b> Polar Covalent	Class <b>D</b> Dimetallacarbene
Chart 1. Distinct Bimetallic $\mu$ -Carbido Bonding Modes. <sup>1-4</sup>			

Whilst an understanding of the bonding within bimetallic carbidos is emerging<sup>1n,3g,4a,4b</sup> their reactivity remains essentially uncharted. Reactivity studies are limited to various co-ligand substitutions,<sup>11,1m,2b,2g,3e,4a</sup>, oxidation to a CO ligand (Class **A**),<sup>11</sup> protonation to afford a  $\mu$ -methylidyne (Class **B**<sup>2b</sup> or **D**<sup>4b</sup>), CS<sub>2</sub>-insertion (Class **B**),<sup>2b</sup> halogenation to afford  $\mu$ -halocarbynes (Class **A**)<sup>1m</sup> and interconversion of bonding classes (Classes **C**  $\rightarrow$  **B**<sup>3e,f</sup> and **A**  $\rightarrow$  **D**<sup>4a</sup>). For Class **D**  $\mu$ -carbidos, the bent geometry at carbon renders it nucleophilic in reactions with various electrophiles (CO<sub>2</sub>, MeOH, chalcogens, metals).<sup>4</sup>

The Class A complex  $[Rh_2(\mu-C)Cl_2(PPh_3)_4]$  (1) is readily accessible via the reaction of  $[RhCl(CS)(PPh_3)_2]$  (2) with

catecholborane<sup>11</sup> however the mechanism of its formation, remains obscure. Attempts to extend this desulfurisation to numerous other rhodium thiocarbonyl complexes or [IrCl(CS)(PPh<sub>3</sub>)<sub>2</sub>] have yet to find success. To generally explore the reactivity of bridging carbido ligands and, more specifically, processes that involving carbon-chalcogen bond cleavage<sup>1d,k,o,2e</sup> or formation,<sup>4b</sup> we now discuss the reactions of dirhodium carbido complexes with CS<sub>2</sub> and chalcogens.

Documented reactions of metal-carbon multiple bonded species with CS<sub>2</sub> are somewhat scarce,<sup>5</sup> being limited to the inferred intermediacy of a thiocarbonyl-carbyne complex *en route* to a thioketenyl;<sup>5a</sup> and the cleavage of CS<sub>2</sub> by the carbyne complexes [Ru(=CPh)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [Mo(=CR)(CO)(L)(Tp)] (R = C<sub>6</sub>H<sub>4</sub>Me-4; L = CO, PPh<sub>3</sub>; Tp = hydrotris(pyrazolyl)borate) to afford the thiobenzoyl complex [Ru(η<sup>2</sup>-SCPh)Cl(CS)(PPh<sub>3</sub>)<sub>2</sub>]<sup>5b</sup> or the thioketene complex [Mo(κ<sup>2</sup>-:η<sup>2</sup>,σ'-SCCRCOS)(=O)(Tp)], respectively.<sup>5c</sup> For carbene complexes, Young has described a thioketene pincer with CS<sub>2</sub> and PPh<sub>3</sub>,<sup>5d</sup> while Bourissou has observed the insertion of CS<sub>2</sub> into a gold(III) carbene complex.<sup>5e</sup>

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

Surprisingly, the product of this reaction was the coordinatively unsaturated *mono*-thiocarbonyl complex  $[Rh_2(\mu-CS)Cl_2(\mu-dppm)_2]$  (**4**, Figure S1), which could also be spectroscopically observed to form when **3** was treated with

<sup>&</sup>lt;sup>a</sup> Research School of Chemistry, Australian National University, Canberra,

Australian Capital Territory, ACT 2601, Australia. Email: a.hill@anu.edu.au Electronic Supplementary Information (ESI) available: Synthetic procedures, spectroscopic and crystallographic data. See DOI: 10.1039/x0xx00000x. 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  $\mu$ -carbido complexes with CS<sub>2</sub> and chalcogens (R = CO<sub>2</sub>Me; *i* = CS<sub>2</sub>, *ii* = HBO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, *iii* = <sup>1</sup>/<sub>8</sub> S<sub>8</sub>, *iv* = <sup>1</sup>/<sub>n</sub> Se<sub>n</sub>, *v* = RC=CR.

elemental sulfur but not with methylthiirane (vide infra) nor when [RhCl(CS)(PPh<sub>3</sub>)<sub>2</sub>] was treated with dppm. The corresponding carbonyl analogue of 4 is well known<sup>8</sup> and the structural features of interest pertaining to the  $Rh_2(\mu$ -CA) (A = O,<sup>8c</sup> 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<sub>2</sub>CS 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: ωB97X-D/6-31G\*/LANL2Dζ, 1.930 and 2.727 Å see ESI) for the hypothetical model complex  $[Rh_2(\mu-CS)Cl_2(\mu-dmpm)_2]$  (dmpm = 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  $Rh(d_{r2})$  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  $\sigma$ -bonding respectively.

For the reactions of both **1** and **3** we envisage initial coordination of CS<sub>2</sub> to one of the coordinatively unsaturated rhodium centres (**E**, Scheme 1)<sup>9</sup> followed by a cyclo-addition with one Rh=C multiple bond *via* a hetero-alkene metathesis mechanism (**F**, Scheme 1).<sup>5b,10</sup> 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 [Rh<sub>2</sub>Cl<sub>2</sub>(CS)<sub>2</sub>(dppm)<sub>2</sub>] (*cf.* the known dicarbonyl analogue<sup>8</sup>), from which dissociation of CS is required to provide **4**. Notably, in

#### **Chemical Communications**

contrast to CO it is extremely rare for thiocarbonyluligands in a simply dissociate, ^11 given the high energy of the CS  $\tt DOCCO5106C$ 

The complex **3** also slowly reacts with elemental selenium to form the a  $\mu_2$ -selenocarbonyl complex [Rh<sub>2</sub>( $\mu$ -CSe)Cl<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>] (**5**, Figure 1). Selenocarbonyl complexes remain rare<sup>11</sup> and group 9 examples are limited to an *isoselenocarbonyl* complex<sup>12a</sup> and those derived from [IrCl(CSe)(PPh<sub>3</sub>)<sub>2</sub>].<sup>12b</sup> 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<sup>11e</sup> CSe complex [Ru<sub>2</sub>( $\mu$ -CSe)( $\mu$ -NPh)( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (1.802(13), 1.844(12) Å).<sup>4b</sup> 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 [Rh<sub>2</sub>( $\mu$ -CA)Cl<sub>2</sub>(dmpm)<sub>2</sub>] (A = O, S, Se; see ESI) indicating the involvement of packing effects.



**Figure 1.** Molecular structure **5** in a crystal of **5**.(PhMe)<sub>1.5</sub> (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–Cl1 1.911(9), Rh2–Cl 1.928(8), Se1–Cl 1.747(8), C1–Rh1–Rh2 43.8(3), Rh2–Cl–Rh1 91.8(4), Se1–Cl–Rh1 134.0(6). Insets: alternative views along and orthogonal to the Rh<sub>2</sub>C plane.

The reactions of terminal carbido complexes with chalcogens have been shown to afford chalcocarbonyl ligands<sup>2d,11e,13</sup> 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  $[Rh_2(\mu-C)Cl_2(\mu-DMAD)(\mu-dppm)_2]$  (6, DMAD = dimethyl acetylenedicarboxylate)<sup>4a</sup> 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  $[Rh_2(\mu-CS)Cl_2(\mu-DMAD)(\mu-dppm)_2]$  (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 methylthiirane<sup>14</sup> led to complete destruction of the complex such that dppm-S and dppm-S2 were the predominant phosphorus-containing products observed (<sup>31</sup>P 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 **Chemical Communications** 

#### COMMUNICATION

the mono-*aquo* complex  $[Rh_2(\mu-CS)Cl_2(OH_2)(\mu-DMAD)(\mu-dppm)_2]$  (**7a**, Figure 2). Similar behaviour was encountered for the trigonal carbido complexes  $[Rh_2M(\mu_3-C)Cl_3(OH_2)(\mu-DMAD)(\mu-dppm)_2]$  (M = Cu, Au) such that while the water molecule does not remain bound in solution, the symmetry reduction ( $C_{2v} \rightarrow C_s$ ) upon coordination of water to a *single* rhodium impacts upon crystallisation.



**Figure 2.** Molecular structure **7a** in a crystal of **7a**.CHCl<sub>3</sub> (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 Rh<sub>2</sub>C plane.

Prior to the advent of **4** and **7a**, structural data for homobimetallic  $\mu$ -thiocarbonyl ligands were somewhat sparse<sup>15</sup> with none available for rhodium. Far more geometric data for bridging chalcocarbonyls have however emerged from extensive computational studies by King and Li.<sup>16</sup> Symmetrical  $\mu$ -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<sup>15a</sup> to 1.629 Å<sup>4b</sup>). 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.<sup>4</sup> To quantify the donor properties of the increasing diversity of NHC ligands, Ganter has proposed employing the <sup>77</sup>Se NMR shift of the corresponding selenone.<sup>17</sup> The "carbene" 6 also reacts slowly with selenium (but not tellurium) to afford inter alia  $[Rh_2(\mu-CSe)Cl_2(\mu-DMAD)(\mu-dppm)_2]$  (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. [Rh<sub>2</sub>(µ-CSe)(OH<sub>2</sub>)Cl<sub>2</sub>(µ-DMAD( $\mu$ -dppm)<sub>2</sub>] (**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<sup>4b</sup> to display the symmetrical bridging mode. The  $v_{CSe}$  infrared absorption is tentatively assigned to a band of medium intensity at 1000 cm<sup>-1</sup><sub>1</sub>( $f_{r_1}$ ( $f_{r_1}$ ( $f_{r_1}$ ( $f_{r_1}$ )( $f_{r_1}$ )), that is absent in the precursor and based/on Redirch-Teller considerations correlates with those found at 1249 cm<sup>-1</sup> for **7** and 1700 cm<sup>-1</sup> for [Rh<sub>2</sub>( $\mu$ -CO)Cl<sub>2</sub>( $\mu$ -DMAD)( $\mu$ -dppm)<sub>2</sub>].<sup>8b</sup> In the infrared spectra of terminal selenocarbonyls, the v<sub>CSe</sub> mode is typically the most intense, however for **5** and **8** these modes are weak, as could be computationally substantiated for the model complexes [Rh<sub>2</sub>( $\mu$ -CSe)Cl<sub>2</sub>L<sub>n</sub>] (L<sub>n</sub> = dmpm, dHpm, (CO)<sub>4</sub>, (CO)<sub>6</sub>) and [Rh<sub>2</sub>( $\mu$ -CSe)( $\mu$ -HCCH)Cl<sub>2</sub>(dmpm)<sub>2</sub>] (v<sub>CSe</sub> : 970-1030 cm<sup>-1</sup>; 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 (1.608-1.786Å)<sup>11,18</sup> and shorter than found in NHCderived selenones (1.82-1.84 Å),<sup>17</sup> or selenoureas, *e.g.*, 1.844(4) Å for(Me<sub>2</sub>N)<sub>2</sub>C=Se.<sup>19</sup>



Figure 3. Molecular structures of 8a in a crystal of 8a.(PhMe)(CH<sub>2</sub>Cl<sub>2</sub>)<sub>0.5</sub>, (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–C11 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 <sup>77</sup>Se NMR derived parameters, we might anticipate that the <sup>77</sup>Se NMR spectrum of **8** comprises a single 15-line (tripled pentet, <sup>103</sup>Rh and <sup>31</sup>P: *I* = ½) resonance at *ca*  $\delta_{se}$ = 530 ppm based on the HOMO-LUMO gap for **6**. Unfortunately, scanning the complete ~3000 ppm range for known selenium shifts failed (as with  $\delta_c$ ) to identify a signal even employing a 133.4 MHz instrument, due to the high order coupling to <sup>103</sup>Rh and <sup>31</sup>P (see ESI).

In conclusion, whilst CS<sub>2</sub> has proven to be a valuable source molecule for the installation of  $\mu$ -carbido ligands in bimetallic complexes,<sup>1d,1h,1n</sup> 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**  $\mu$ -carbido complex has allowed the construction of CS and CSe complexes further reinforcing the Class **D**/NHC analogy to provide the first rhodium selenocarbonyls.

#### Acknowledgements

6

#### COMMUNICATION

Page 4 of 5

We gratefully acknowledge the Australian Research Council (DP170102695 and DP190100723) for funding. The authors declare no conflicts.

#### Notes and references

- 1 Class A: (a) D. Mansuy, J. P. Lecomte, J. C. Chottard and J. F. Bartoli, Inorg. Chem., 1981, 20, 3119-3121. (b) R. L. Miller, P. T. Wolczanski and A. L. Rheingold, J. Am. Chem. Soc., 1993, 115, 10422-10423. (c) E. Solari, S. Antonijevic, S. Gauthier, R. Scopelliti and K. Severin, Eur. J. Inorg. Chem., 2007, 367-371. (d) R. D. Young, A. F. Hill, G. E. Cavigliasso and R. Stranger, Angew. Chem. Int. Ed., 2013, 52, 3699-3702. (e) G. Rossi, V. L. Goedken and C. Ercolani, Chem. Commun., 1988, 46-47. (f) A. Kienast and H. Homborg, Z. Anorg. Allg. Chem., 1998, 624, 107-112. (g) C. Colomban, E. V. Kudrik, D. V. Tyurin, F. Albrieux, S. E. Nefedov, P. Afanasiev and A. B. Sorokin, Dalton Trans., 2015, 44, 2240 - 2251. (h) W. Beck, W. Knauer and C. Robl, Angew. Chem., Int. Ed., 1990, 29, 318-320. (i) A. F. Hill and L. J. Watson, Chem. Commun., 2020, 56, 2356-2359. (j) H. J. Barnett, L. K. Burt and A. F. Hill, Dalton Trans., 2018, 47, 9570-9574. (k) H. J. Barnett and A. F. Hill, Chem. Commun., 2019, 55, 1734-1737. (I) H. J. Barnett and A. F. Hill, Chem. Commun., 2020, 56, 2356-2359. (m) T. Ahrens, B. Schmiedecke, T. Braun, R. Herrmann and R. Laubenstein, Eur. J. Inorg. Chem., 2017, 713-722.
- Class B: (a) S. L. Latesky and J. P. Selegue, J. Am. Chem. Soc., 1987, 109, 4731-4733. (b) M. Etienne, P. S. White and J. L. Templeton, J. Am. Chem. Soc., 1991, 113, 2324-2325. (c) A. F. Hill, M. Sharma and A. C. Willis, Organometallics, 2012, 31, 2538-2542. (d) R. L. Cordiner, A. F. Hill and J. Wagler, Organometallics, 2008, 27, 5177-5179. (e) I. A. Cade, A. F. Hill and C. M. A. McQueen, Organometallics, 2009, 28, 6639-6641. (f) W. Knauer, W. Beck Z. Anorg. Allg. Chem., 2008, 634, 2241-2245. (g) E. S. Borren, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, J. Am. Chem. Soc., 2013, 135, 4942-4945. (h) A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang and A. C. Willis, Organometallics, 2009, 28, 4394-4399. (i) L. K. Burt, R. L. Cordiner, A. F. Hill, R. A. Manzano and J. Wagler, Chem. Commun., 2020, 56, 5673-5676. (j) L. K. Burt and A. F. Hill, Dalton Trans., 2020, 49, 8143-8161.
- Class C: (a) A. Hejl, T. M. Trnka, M. W. Day and R. H. Grubbs, *Chem. Commun.*, 2002, 2524-2525. (b) A. Reinholdt, K. Herbst and J. Bendix, *Chem. Commun.*, 2016, **52**, 2015-2018. (c) A. Reinholdt, J. E. Vibenholt, T. J. Morsing, M. Schau-Magnussen, N. E. A. Reeler and J. Bendix, *Chem. Sci.*, 2015, **6**, 5815-5823. (d) A. Reinholdt and J. Bendix, *Inorg. Chem.*, 2017, **56**, 12492-12497. (e) A. Reinholdt, A. F. Hill and J. Bendix, *Chem. Commun.*, 2018, **54**, 5708-5711. (f) A. Reinholdt, J. Bendix, A. F. Hill and R. A. Manzano, *Dalton Trans.*, **2018**, *47*, 14893-14896.
- 4 Class D: (a) H. J. Barnett and A. F. Hill, Angew. Chem., Int. Ed., 2020, 59, 4272-4277. (b) S. Takemoto, J. Ohata, K. Umetani, M. Yamaguchi and H. Matsuzaka, J. Am. Chem. Soc., 2014, 136, 15889-15892. (c) S. Takemoto, H. Ishii, M. Yamaguchi, A. Teramoto, M. Tsujita, D. Ozeki and H. Matsuzaka, Organometallics, 2019, 38, 4298-4306. (d) S. Takemoto, M. Tsujita and H. Matsuzaka, Organometallics, 2017, 36, 3686-3691.
- 5 (a) T.-Y. Lee and A. Mayr, J. Am. Chem. Soc., 1994, 116, 10300-103001. (b) R. B. Bedford, A. F. Hill, A. J. P. White and D. J. Williams, Angew. Chem., Int. Ed., 1996, 35,95-97. (c) A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, Inorg. Chem., 1998, 37, 598-600. (d) S. Sung, T. Joachim, T. Kramer and R. D. Young, Organometallics, 2017, 36, 3117-3124. (e) A. Pujol, M. Lafage, F. Rekhroukh, N. Saffon-Merceron, A. Amgoune, D.

Bourissou, N. Nebra, M. Fustier-Boutignon and N. Metzalles. Angew. Chem., Int. Ed., 2017, **56**, 12264,1226739/DOCCO5106C (a) M. C. Baird and G. Wilkinson, Chem. Commun., 1966, 267-

- 268.
  7 (a) C. P. Kubiak and R. Eisenberg, J. Am. Chem. Soc. 1977, 99, 6129-6131.
- 8 (a) M. Cowie and S. K. Dwight, *Inorg. Chem.*, 1980, 19, 2500-2507. (b) L. Gelmini, D. W. Stephan and S. J. Loeb, *Inorg. Chim. Acta*, 1985, 98, L3-L6.
- 9 (a) M. Doux, N. Mezailles, L. Ricard and P. Le Floch, Organometallics, 2003, 22, 4624-4626; (b) C. Bianchini, D. Masi, C. Mealli, A. Meli and M. Sabat, Organometallics, 1985, 4, 1014-1019; (c) E. Lindner, B. Keppeler, H. A. Mayer, K. Gierling, R. Fawzi and M. Steimann, J. Organomet. Chem., 1996, 526, 175-183; (d) R. H. Lam, C. M. A. McQueen, I. Pernik, R. T. McBurney, A. F. Hill and B. A. Messerle, Green Chem., 2019, 21, 538-549.
- (a) J-L Hérisson and Y. Chauvin, *Makromol. Chem.* Phys., 1971, 141, 161–176.
   (b) A. F. Hill, *J. Mol. Cat.*, 1991, 65, 85-93.
- (a) I. S. Butler, Acc. Chem. Res., 1977, 10, 359-365. (b) P. V. Broadhurst, Polyhedron, 1985, 4, 1801-1846. (c) W. Petz, Coord. Chem. Rev., 2008, 252, 1689-1733. (d) Y. Mutoh, N. Kozono, K. Ikenaga and Y. Ishii, Coord. Chem. Rev., 2012, 256, 589-605. (e) B. J. Frogley, A. F. Hill and L. J. Watson, Chem. Eur. J. 10.1002/chem.202001588.
- (a) A. F. Hill and C.M. A. McQueen Organometallics, 2012, 31, 2482-2485;
   (b) W. R. Roper and K. G. Town, J. Organomet. Chem., 1983, 252, C97-C100.
- 13 (a) J. B. Greco, J. C. Peters, T A. Baker, W. M. Davis, C. C. Cummins and G. Wu, *J. Am. Chem. Soc.*, 2001, **123**, 5003-5013; (b) Y. Mutoh, N. Kozono, M. Araki, N. Tsuchida, K. Takano and Y. Ishii, *Organometallics*, 2010, **29**, 519-522. (c) B. B. J. Frogley, A. F. Hill, C. S. Onn and L. J. Watson, *Angew. Chem., Int. Ed.*, 2019, **58**, 15349-15353. (d) B. J. Frogley, A. F. Hill and L. J. Watson, *Dalton Trans.*, 2019, **48**, 12598-12606
- 14 (a) D. J. Cook and A. F. Hill, *Organometallics*, 2003, 22, 3502-3512. (b) D. J. Cook and A. F. Hill, *Chem. Commun.*, 1997, 955-956.
- (a) H. Werner, O. Kolb, U. Schubert and K. Ackermann, J. Organomet. Chem., 1982, 240, 421-428; (b) D. E. Beckman and R. A. Jacobson, J. Organomet. Chem., 1979, 179, 187-196; (c) V. G. Albano, S. Bordoni, L. Busetto, A. Palazzi, P. Sabatino and V. Zanotti, J. Organomet. Chem., 2002, 659, 15-21; (d) H. Adams, L. V. Y. Guio, M. J. Morris and A. J. Pratt, J. Chem. Soc., Dalton Trans., 2000, 3489-3490; (f) V. G. Albano, S. Bordoni, L. Busetto, C. Camiletti, M. Monari, A. Palzzi, F. Prestopino and V. Zanotti, J. Chem. Soc., Dalton Trans., 1997, 4665-4670.
- 16 (a) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King, *Inorg. Chim. Acta* 2011, 375, 193-204; (b) A. Peng, X. Zhang, Q.-S. Li, R. B. King, H. F. Schaefer III, *New J. Chem.* 2013, 37, 775-783; (c) Z. Zhang, L. Pu, Q.-S. Li, R. B. King, *New J. Chem.* 2014, 38, 4282-4289; (d) H. Gong, Q. Luo, Q.-S. Li, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.* 2015, 54, 132-142.
- 17 K. Verlinden, H. Buhl, W. Frank and C. Ganter, *Eur. J. Inorg. Chem.*, 2015, 2416-2425.
- 18 (a) B. J. Frogley, A. F. Hill and L. J. Watson, *Chem. Commun.*, 2019, **55**, 14450-14453; (b) B. J. Frogley, A. F. Hill, C. S. Onn and L. J. Watson, *Angew. Chem., Int. Ed.*, 2019, **58**, 15349-15353; (c) B. J. Frogley, A. F. Hill and L. J. Watson, *Dalton Trans.*, 2019, **48**, 12598-12606; (d) A. F. Hill and L. J. Watson, *Chem. Commun.*, 2020, **56**, 2356-2359; (e) I. A. Cade, A. F. Hill and C. M. A. McQueen, *Dalton Trans.* 2019, **48**, 2000-2012; (f) B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun.*, 2018, **54**, 1702-1705; (g) L. M. Caldwell, A. F. Hill, J. Wagler and A. C. Willis, *Dalton Trans.*, 2008, 3538-3541.
- 19 M. P. Campos, M. P. Hendricks, A. N. Beecher, W. Walravens, R. A. Swain, G. T. Cleveland, Z. Hens, M. Y. Sfeir and J. S. Owen, *J. Am. Chem. Soc.*, 2017, **139**, 2296-2305.

Published on 04 September 2020. Downloaded on 9/6/2020 6:59:22 AM.

## **Table of Contents Text**

Different classes of dirhodium  $\mu$ -carbido complexes cleave CS<sub>2</sub> to afford mono- and binuclear CS complexes, the CSe analogues of which are also described.

### **Table of Contents Graphic**

