# Thiocarbonylphosphorane and Arsorane Ligands

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Independently unstable thiocarbonylphosphorane or arsorane ligands S=C=AR$_3$ (A = P, As) are observed in the salts [W(η^2-*C,S*-SCAR$_3$)(CO)$_2$(Tp*)]PF$_6$ [AR$_3$ = PCy$_3$, PMe$_n$Ph$_{3-n}$: n = 0, 1, 2, AsMePh$_2$; Tp* = tris(dimethylpyrazolyl)borate] which arise from the reactions of phosphoniocarbynes [W($\equiv$CAR$_3$)(CO)$_2$(Tp*)]$^+$ with sulfur.

The coupling of ligands underpins the synthetic utility of organotransition metal chemistry, encompassing *inter alia* reductive elimination, migratory insertion and alkene/alkyne metathesis processes. Perhaps the two most ubiquitous ligands in organometallic chemistry are carbon monoxide (CO) and phosphines (PR$_3$). Many thousands of complexes are known to contain both and so it might be expected, were it plausible, that by now the coupling of phosphine and carbonyl ligands might have been observed. In isoelectronic terms, migration of a σ-silyl ligand to a carbonyl, isonitrile[1] or thiocarbonyl,[2] whist rare, has on occasion been observed, as has the insertion of CO into a metal phosphido bond (Scheme 1).[3]
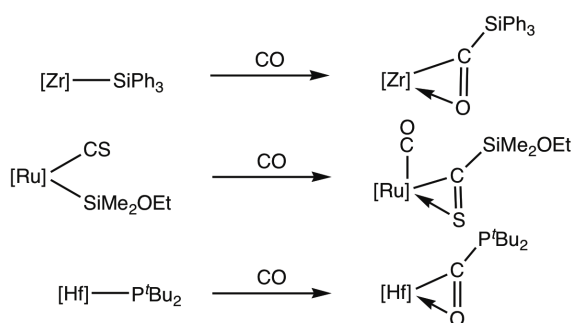
Scheme 1: Heteroacyls. [Zr] = ZrCl(C$_5$Me$_5$)$_2$,[1] [Ru] = RuCl(PPh$_3$)$_2$,[2] [Hf] = HfCl$_2$(C$_5$Me$_5$).[3]

These archetypal examples have in common that the resulting heteroacyl adopts a bidentate coordination mode that satisfies not only the effective atomic number requirements of the metal but also its HSAB proclivities. Thus the CO examples involve early, hard (oxophilic) d^0 metal centres, while 'metallathiirenes' (Chart 1b)[4] are favoured for later soft transition metals.[5]
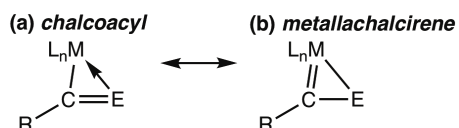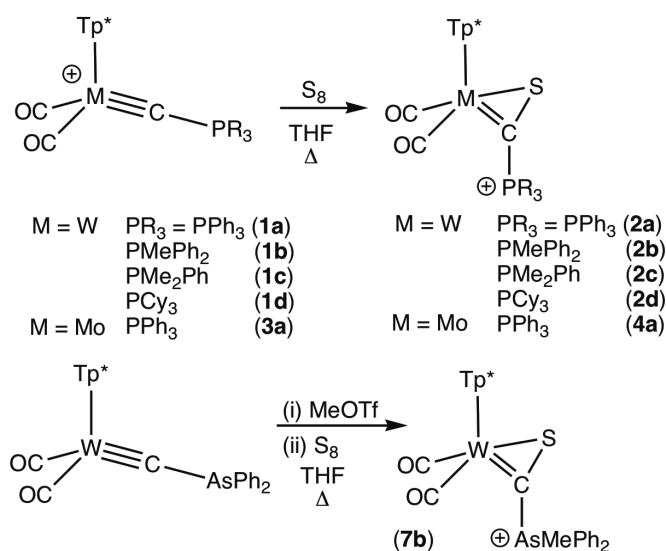

Chart 1: Canonical Descriptions of Heteroacyl Bonding: (a) Chalcoacyl *vs* (b) metallachalcirene (E = O, S, Se, Te).

The products of the coupling of PR$_3$ and CO ligands would be phosphonioacyls (carbonylphosphoranes) and whilst neither these nor mononuclear *thiocarbonyl*phosphoranes are known,[6] phosphaketene RP=C=O complexes have been described from phosphinidene/carbonyl coupling[7] and a single phosphorylthioacyl complex has been reported.[8] Accordingly, we report herein the synthesis of the first examples of thiocarbonylphosphorane (SCPR$_3$) and thiocarbonylarsorane (SCAsR$_3$) complexes.

The homologues Ph$_3$P=C=C=E (E = O, S) are well known, isolable, stable and synthetically versatile reagents,[9a,b] as are the less widely explored bis(phosphonio)chalcocarbonyls (Ph$_3$P)$_2$C=E (E = S, Se).[9c] In contrast, there are no known examples of R$_3$P=C=E and computational optimisation (DFT: ωB97X-V/6-31G*/LANL2Dζ) of the hypothetical molecules Me$_3$P=C=E (E = O, S, Se, Te) in all cases returned geometries with a single imaginary vibrational frequency corresponding to oscillation of the ylidic carbon orthogonal to the P$\cdots$E vector. Similar analysis at this level of theory provided satisfactory geometries for the extended molecules R$_3$P=C=C=E (R = H, Me; E = O, S) as well as (Me$_3$P)$_2$CS (see ESI†).

The nucleophilicity of the chalcocarbonylates [M(CE)(CO)$_2$(Tp*)]$^-$ (M = Mo, W; E = S, Se, Te; Tp* = hydrotris(3,5-dimethylpyrazolyl)borate)[10] has been exploited for the synthesis of isochalcocarbonyl[11] and μ-carbido complexes[12] as well as novel carbon chalcogenide ligands, *e.g.*, CCS, CTeC, CTeTeC.[13] We therefore sought a complementary set of *electrophilic* chalcocarbonyl complexes, *e.g.*, [W(CE)(CO)$_2$(PR$_3$)(Tp*)]$^+$, which are heavier congeners of the known carbonyl complexes [W(CO)$_3$(PR$_3$)(Tp*)]$^+$ (PR$_3$ = PMe$_3$, PEt$_3$, PPh$_3$, PMe$_2$Ph).[14] We anticipated (incorrectly) that addition of chalcogens across the W$\equiv$C multiple bond[4e-g,15] of the readily available phosphoniocarbyne salts [W($\equiv$CPR$_3$)(CO)$_2$(Tp*)]PF$_6$ (PR$_3$ = PPh$_3$ **1a**, PMePh$_2$ **1b**, PMe$_2$Ph **1c**, PCy$_3$ **1d**)[8,16] would be accompanied by migration of the phosphine to tungsten. In practice, the reactions of these phosphoniocarbynes with elemental sulfur results in the formation of intense blue salts [W(η^2-SCPR$_3$)(CO)$_2$(Tp*)]PF$_6$ (PR$_3$ = PPh$_3$ **2a**, PMePh$_2$ **2b**, PMe$_2$Ph **2c**, PCy$_3$ **2d**, Scheme 2).

Scheme 2: Synthesis of Thiocarbonylphosphorane and Arsorane Complexes.

Table 1. Selected Spectroscopic Data for the Complexes $[M(SCAR_3)(CO)_2(Tp^*)]^+$

	M	AR$_3$	$\nu_{CO}{}^a$ [cm^{-1}]	$k_{CO}{}^b$ [Ncm^{-1}]	$\delta_C(SC)^c$ [ppm]	$^1J_{PC}$ [Hz]	$\delta_P{}^c$ [ppm]
2a	W	PPh$_3$	2006	1919	15.53	220.7^d	54	26.8^e
2b	W	PMePh$_2$	1998	1914	15.43	219.0	56	26.4^f
2c	W	PMe$_2$Ph	1999	1912	15.42	222.3^g	56	30.4^h
2d	W	PCy$_3$	1996	1911	15.39	222.7^g	30	42.0^i
4a	Mo	PPh$_3$	2016	1936	15.75	235.5	45	21.0
7b	W	AsMePh$_2$	1999	1905	15.37	226.0^j	–	–

^{a}Measured in CH$_2$Cl$_2$. ^{b}Cotton-Kraihanzel force constant. ^{c}Measured in CD$_2$Cl$_2$. ^{d} $^1J_{CW}$ = 46 Hz. ^{e} $^2J_{PW}$ = 91 Hz. ^{f} $^2J_{PW}$ = 21 Hz. ^{g} $^1J_{CW}$ = 45 Hz ^{h} $^2J_{PW}$ = 20 Hz. ^{i} $^2J_{PW}$ not resolved. ^{j} $^1J_{CW}$ = 41 Hz.

While formation of **2a-c** was essentially complete within 6 hours in refluxing tetrahydrofuran, the more sterically encumbered PCy$_3$ derivative **1d** required 18 hours for significant (*ca* 80%) formation of **2d**, and this was accompanied by the onset of decomposition, with only ca 90% purity being achieved after chromatography. The formulation as thiocarbonylphosphorane rather than thiocarbonyl-phosphine complexes was immediately suggested by the absence of an infrared ν_{CS} absorption in the 1200-1350 cm^{-1} region[17] and the striking blue colours, reminiscent of those for thioaroyl[4f-5] and selenoaroyl[15] complexes. The formulation was confirmed from a combination of ^{13}C{^{1}H} NMR data (Table 1) and crystallographic analyses of **2a** (ESI†) and **2b** (Figure 1).

The phosphines chosen provide a spread of Tolman electronic parameters from ν^T = 2068.9 (PPh$_3$) to 2056.4 cm^{-1} (PCy$_3$),[18] however this variation in basicity is only mildly transmitted to the tungsten centre or the thioacyl carbon, as reflected in infrared (ν_{CO}) data. The values of $^1J_{PC}$ and $^2J_{WP}$ are rather invariant with the exception of the PCy$_3$ derivative for which both are significantly reduced, perhaps accounting for this derivative being the least stable. Most likely, this reflects an approach to the limit of steric bulk that may be easily accommodated around the 'CS' unit. In this context we note that **2d** is unique in that on ambient storage in solution, reformation of the W≡C multiple bond in **1d** slowly ensues.
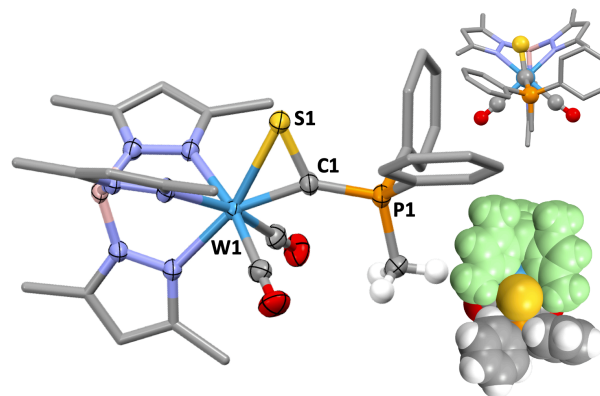

Figure 1: Molecular structure of the cation of **2b** in a crystal of **2b**.2MeCN (50% displacement ellipsoids, pyrazolyl and phenyl rings simplified. Solvent, hydrogens and PF$_6$ anion omitted). Selected bond lengths (Å) and angles (°): W1–S1 2.5638(8), W1–C1 1.978(3), S1–C1 1.716(3), P1–C1 1.767(3), C1-W1-S1 41.98(9), S1-C1-W1 87.61(13), S1-C1-P1 124.74(18), P1-C1-W1 147.24(19). Insets: View along C1-W1 vector and space-filling representation (Tp* green)

The molecular structure of the cationic complex of **2b** in the solid state (Figure 1) reveals that the W1–C1 (1.978(3) Å) and C1–S1 (1.716(3) Å) bond lengths indicate a degree of multiple bonding, while the W1–S1 bond length of 2.5638(8) Å is somewhat long relative to thiolato ligands bound to seven-coordinate tungsten.[19] Taken together, these indicate that both valence bond forms (Chart 1) contribute to the overall description, with perhaps the metallathiirene being particularly apt. This is borne out by computational interrogation of the model complex[20] $[W(\eta^2\text{-SCPMe}_3)(CO)_2(Tp)]^+$ (**2^S**: Tp = hydrotris(pyrazolyl)borate, DFT:ωB97X-V/LANL2Dζ/gas phase, Figure 2) which provides Löwdin bond orders of 1.037, 1.23 and 1.61 for the W–S, C–S and W–C bonds, respectively.

The HOMO for **2^S** comprises the W-C multiple bond in antibonding combination with a sulfur 'lone pair' while HOMO—9 represents the fully delocalised π-bonding of the metallathiirene. Accordingly, the sulfur would appear to present the most nucleophilic site, as substantiated by the atom-condensed Fukui functions (f^-, Table 2) for W (0.174), C (≈0) and S (0.260). The LUMO involves considerable metallathiirene carbon character while the more multicentred LUMO+1 has substantial carbonyl contribution suggesting both sites may be susceptible to nucleophilic attack, though the f^+ indices for the CS (0.14) and CO (0.02) carbon atoms would favour the former. The conspicuous intense blue colours of the

SCPR$_3$ complexes (CH$_2$Cl$_2$: λ_{max} = 627 **2a**, 622 **2b**, 627 **2c**, 627 nm **2d**) may be traced (TD-DFT analysis of **2^S**) primarily to HOMO→LUMO (Calc. 607 nm), HOMO→LUMO+1 and HOMO-1→LUMO (Calc. 452, 456 nm) transitions, each of which has significant LMCT character.

Table 2. Calculated^a Atom-Condensed Fukui Functions ($f\pm$) and Natural Atomic Charges (Z) for the Hypothetical Complexes [W(η^2-ECPMe$_3$)(CO)$_2$(Tp*)]$^+$ (E = O, S)

E	f^+(W)	f^+(C)	f^+(E)	f^-(W)	f^-(C)	f^-(E)	Z(W)	Z(C)	Z(E)
O	0.17	0.20	0.07	0.27	0.03	0.15	1.00	-0.40	-0.66
S	0.21	0.14	0.14	0.17	0.03	0.26	1.08	-0.92	-0.09

^{a}DFT:ωB97X-X/6-31G*/LANL2Dζ(W)/gas phase.
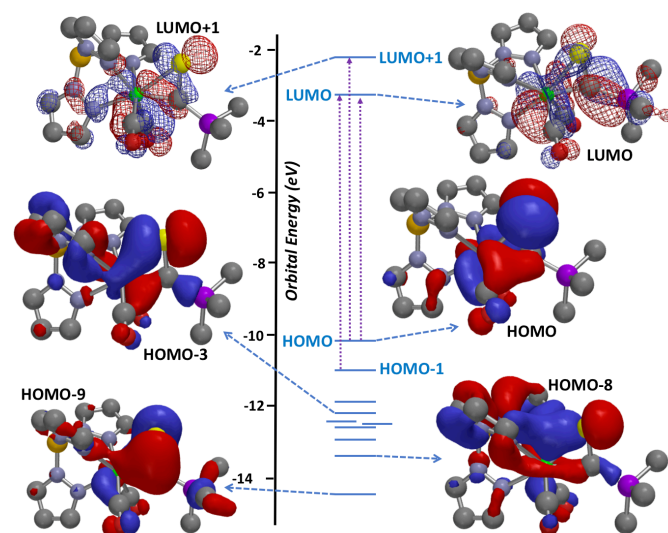
Figure 2. Frontier orbitals and electronic transitions of interest for the model complex [W(η^2-SCPMe$_3$)(CO)$_2$(Tp)]$^+$ (**2^S**, DFT:ωBP87X-V/6-31G*/LANL2Dζ(W)/gas phase)

Elaboration of the thiocarbonylphosphorane motif beyond the present system was explored with respect to the metal, chalcogen and pnictogen. Molybdenum phosphoniocarbynes are presently unknown,[21] however the salt [Mo(≡CPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (**3a**) was readily prepared by analogy with **1a**, structurally characterised (ESI†) and converted without issue to [Mo(η^2-SCPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ (**4a**). Other than changes expected for replacement of tungsten by molybdenum the spectroscopic data for **4a** (Table 1) conform to those for **2a**. Attempts to prepare the corresponding selenocarbonyl-phosphorane [W(η^2-SeCPPh$_3$)(CO)$_2$(Tp*)]PF$_6$ from **1a** and grey selenium in THF failed to discern any conversion over 1 week under reflux. Most likely, this is due to the poor solubility of grey selenium, given that stable selenoaroyl complexes, *e.g.*, [Mo(η^2-SeCC$_4$H$_3$S-2)(CO)$_2$(Tp)][15] and [Os(η^2-SeCC$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$][22] are known. Rauchfuss has championed the use of *N*-methylimidazole (NMI) for activating selenium[23] and accordingly the complex **1c** was treated with selenium and a small excess of NMI in refluxing THF. Whilst an intense blue colour developed consistent with the formation of [W(η^2-SeCPMe$_2$Ph)(CO)$_2$(Tp*)]PF$_6$ (**5c**), this defied isolation. Finally, a thiocarbonylarsorane was targeted, however treating [W(≡CBr)(CO)$_2$(Tp*)] with AsPh$_3$ under conditions employed for phosphoniocarbyne syntheses failed to result in any observable

conversion, perhaps reflecting the reduced nucleophilicity of arsines *cf.* phosphines. The first arsoniocarbye [W(≡CAsMePh$_2$)(CO)$_2$(Tp*)]OTf (**6b**) was only recently obtained *via* methylation of the *arsino*carbyne [W(≡CAsPh$_2$)(CO)$_2$(Tp*)].[24] This salt was found to react with sulfur to provide the thiocarbonylarsorane [W(η^2-SCAsMePh$_2$)(CO)$_2$(Tp*)]OTf (**7b**), IR and ^{13}C NMR data for which are comparable to those for **2b** (other than the expected absence of $^1J_{PC}$ and δ_P).

Having established the viability of the ECAR$_3$ moiety as a ligand, the question arises as to why these have yet to arise from the coupling of chalcocarbonyl and phosphine or arsine ligands. In thermodynamic terms, it is instructive to consider the pairs of complexes [W(CE)(CO)$_2$(PMe$_3$)(Tp)]$^+$ (E = O **8°**, S **8^S**, Se **8^{Se}**, Te **8Te**, NMe **8^{NMe}**) and [W(η^2-ECPMe$_3$)(CO)$_2$(Tp)]$^+$ (E = O **2^O**, S **2^S**, Se **2^{Se}**, Te **2Te**, NMe **2^{NMe}**). Given the quite different dipoles in the gas phase for the isomers **8^S** (2.71 D) and **2^S** (6.17 D) and that the complexes **2a**-**d** form in polar THF, the calculations were performed using a polarization continuum model (ε = 7.43). The energies of the isomers are depicted in Figure 3 from which it is clear that the chalcocarbonylphosphorane complexes **2^S**, **2^{Se}** and **2Te** are more stable than their corresponding chalcocarbonyl-phosphine isomers **8^S**, **8^{Se}** and **8Te** by 7.3, 15.5 and 24.0 kcalmol^{-1}, respectively. In contrast the carbonylphosphorane complex **2^O** is considerably *higher* in energy (25.6 kcalmol^{-1}) than **8°**. The isonitrilephosphorane **2^{NMe}** is similarly less stable than the isonitrile-phosphine complex **8^{NMe}** by 14.6 kcalmol^{-1}. This may be traced primarily to the increasingly strong W–S/Se/Te interaction as might be expected from HSAB considerations. *Dihapto* acyl ligands[25] typically have weak metal-oxygen bonding to any but the most oxophilic (often d^0) metals, while iminoacyls have somewhat stronger M–N bonding.[26] It should also be noted that metal-carbon bond strength increases for M–CO < M–CS < M–CSe < M–CTe, and this is sacrificed upon migration *in silico* to the chalcocarbonyl. Based on Cotton-Kraihanzel force constants for the two carbonyl spectator ligands (Table S2, ESI†), the notional coupling of CE and phosphine ligands results in an increase in the metal π-basicity, i.e., is reductive in nature, while the net acceptor capacity of the ligands ECPMe$_3$ increases in the series CE = CNMe < CO < CS < CSe < CTe.

In conclusion, while chalcocarbonylphosphoranes or arsoranes ECAR$_3$ (E = S, Se; A = P, As) appear to be independently unstable and have not been previously observed, it is possible to construct examples of these ligands at a metal centre, where they show no tendency to cleave to the corresponding chalcocarbonyl and phosphine ligands. Phosphonioacyl (carbonylphosphorane) ligands OCPR$_3$ and their isonitrile analogues, however, appear to be thermodynamically disfavoured relative to carbonyl/isonitrile-phosphine isomers.

Acknowledgements
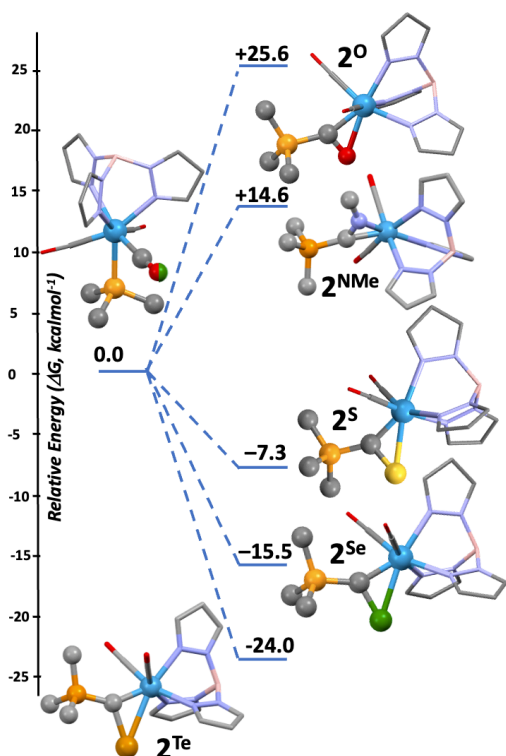
Figure 3. Relative energies (kcalmol⁻¹) and optimised geometries for isomeric chalcocarbonyl-Phosphine [W(CE)(CO)₂(PMe₃)(Tp)]⁺ (8ᴱ) and chalcocarbonylphosphorane [W(η²-ECPMe₃)(CO)₂(Tp)]⁺ (2ᴱ) complexes (E = O, A, Se, Te, NMe; DFT: ωB97X-V/6-31G*/LANL2Dζ(W, Se, Te)/THF).

Notes and references

1 (*a*) T. D. Tilley, *J. Am. Chem. Soc.*, 1985, **107**, 4084-4085. (*b*) H. G. Woo, W. P. Freeman and T. D. Tilley, *Organometallics*, 1992, **11**, 2198-2205.

2 (*a*) C. E. F. Rickard, W. R. Roper, D. M. Salter and L. J. Wright, *Organometallics*, 1992, **11**, 3931-3933. (*b*) M. T. Attar-Bashi, C. E. F. Rickard, W. R. Roper, L. J. Wright and S. D. Woodgate, *Organometallics* **1998**, *17*, 504-506.

3 D. M. Roddick, D. Satarsiero and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 4670-4678.

4 (*a*) G. R. Clark, T. J. Collins, K. Marsden and W. R. Roper, *J. Organomet. Chem.* 1983, **259**, 215-232 (*b*) C. E. F. Rickard, W. R. Roper, S. D. Woodgate and L. J. Wright *J. Organomet. Chem.*, 2001, **623**, 109-115. (*c*) W. Andon, T. Ohtaki, T. Suzuki and Y. Kabe, *J. Am. Chem. Soc.*, 1991, **113**, 7782-7784. (*d*) S. Anderson, D. J. Cook and A. F. Hill, *Organometallics* 2001, **20**, 2468-2476. (*e*) D. J. Cook and A. F. Hill, *J. Chem. Soc., Chem. Commun.* 1997, 955-956. (*f*) D. J. Cook and A. F. Hill, *Organometallics,* 2003, **22**, 3502-3512. (*g*) R. B. Bedford, A. F. Hill, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 95-97. (*h*) R. Drews, F. Edelmann and U. Behrens, *J. Organomet. Chem.*, 1986, **315**, 369-382.

5 J. C. Green, A. L. Hector, A. F. Hill, S. Lin and J. D. E. T. Wilton-Ely, *Organometallics*, 2008, **27**, 5548-5558.

6 A small number of bi- or polymetallic complexes of thiocarbonylphosphoranes have been isolated: (*a*) D. Miguel, D. Morales, V. Riera, S. Garcia-Granda, *Angew. Chem., Int. Ed.*, 2002, **41**, 3034-3036. (*b*) J. Li, D. Miguel, D. Morales, V. Riera, A. Aguirre-Perez and S. Garcia-Granda, *Dalton Trans.*, 2003, 3264-3269. (*c*) H.-F. Klein, A. Schmidt, U. Florke and H.-J. Haupt, *Angew. Chem., Int. Ed.*, 1998, **37**, 2385-2387.

7 A. Grundmann, M. B. Sárosi, P. Lönnecke and E. Hey-Hawkins *Eur. J. Inorg. Chem.,* 2014, 2997-3001.

8 A. L. Colebatch, A. F. Hill, M. Sharma, *Organometallics*, 2015, **34**, 2165-2182.

9 (*a*) C. N. Matthews and G. H. Birum, *Accts. Chem. Res.*, 1969, **2**, 373-379. (*b*) U. Belluco, R. A. Michelin, M. Mozzon, R. Bertani, G. Facchin, L. Zanotti and L. Pandolfo, *J. Organomet. Chem.*, 1998, **557**, 37-68. (*c*) H. Schmidbaur, C. E. Zybill and D. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 310-311.

10 T. Desmond, F.J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc. Chem. Commun.*, 1984, 75-77.

11 (*a*) I. A. Cade, A. F. Hill and C. M. A. McQueen, *Dalton Trans.*, 2019, **48**, 2000-2012. (*b*) L. M. Caldwell, A. F. Hill, J. Wagler and A. C. Willis, *Dalton Trans.*, 2008, 3538-3541. (*c*) L. M. Caldwell, A. F. Hill, A. D. Rae and A. C. Willis, *Organometal-lics*, 2008, **27**, 341-345. (*d*) L. M. Caldwell, R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2010, **29**, 1526-1529. (*e*) A. F. Hill andC. M. A. McQueen, *Organometallics*, 2012, **31**, 2482-2485.

12 (*a*) I. A. Cade , A. F. Hill and C. M. A. McQueen, *Organometal-lics*, 2009, **28**, 6639-6641. (*b*) A. F. Hill and L. J. Watson, *Chem. Commun.*, 2020,**56**, 2356-2359.

13 (*a*) B. J. Frogley, A. F. Hill, C. S. Onn and L. J. Watson, *Angew. Chem., Int. Ed.*, 2019, **58**, 15349-15353. (*b*) L. M. Caldwell, R. Stranger, R. N. L. Terrett, K. M. von Nessi, J. S. Ward and A. C. Willis, *Organometallics* 2015, **34**, 328–334. (*c*) B. J. Fogley, A. F. Hill and L. J. Watson, *Chem. Eur. J.*, 2019, **26**, 12706-12716.

14 C. C. Philipp, P. S. White and J. L. Templeton, *Inorg. Chem.*, 1992, **31**, 3825-3830.

15 L. M. Caldwell, A. F. Hill and A. C. Willis, *Chem. Commun.*, 2005, 2615-2617.

16 (*a*) G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 1954-1959. (*b*) C. S. Onn, A. F. Hill and A. Olding, *Dalton Trans.*, 2020,**49**, 12731-12741.

17 W. Petz, *Coord. Chem. Rev.*, 2008, **252**, 1689-1733.

18 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313-348.

19 (*a*) S. Ludwig, K. Helmdach, M. Huttenschmidt, E. Oberem, J. Rabeah, A. Villinger, R. Ludwig and W. W. Seidel, *Chem. Eur. J.*, 2020, **26**, 16811-16817. (*b*) P. J. Lim, D. A. Slizys, J. M. White, C. G. Young and E. R. T. Tiekink, *Organometallics* 2003, **22**, 4853-4860. (c) C. J. Adams, A. Baber, S. Boonyuen, N. G. Connelly, B. E. Diosdado, A. Kantacha, A. G. Orpen and E. Patrón, *Dalton Trans.* 2009, 9746-9758.

20 The insensitivity of spectroscopic data to variations in phosphines for **2a-c** suggest employing PMe₃ in these calculations is unlikely to perturb the results significantly. Replacing Tp* with Tp for computational economy has been quantified elsewhere: B. J. Frogley, A. F. Hill and R. M. Kirk, *Chem. Commun.,* 2021,**57**, 8770-8773

21 A. L. Colebatch, B. J. Frogley, A. F. Hill and C. S. Onn, *Chem. Eur. J.*, 2021, **27**, 5322-5343.

22 G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.*, 1980, **102**, 6570-6571.

23 T. B. Rauchfuss, *Inorg. Chem.*, 2004, **43**, 14-26.

24 B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2022, **51**, 1907-1917.

25 (*a*) C. A. Rusik, M. A. Collins, A. S. Gamble, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1989, **111**, 2550-2560. (*b*) S. Trofimenko, *J. Am. Chem. Soc.*, 1969, **91**, 588-595. (*c*) M. D. Curtis, K.-B. Shiu and W. M. Butler, *Organometallics*, 1983, **2**, 1475-1477. (*d*) E. Carmona, L. Sanchez, J. M. Marin, M. L. Poveda, J. L. Atwood, R. D. Priester and R. D. Rogers, *J. Am. Chem. Soc.*, 1984, **106**, 3214-3222.

26 (*a*) W. R. Roper, G. E. Taylor, J. M. Waters and L. J. Wright, *J. Organomet. Chem.,* 1978, **157**, C27-C29. (*b*) R.D. Adams and D.F. Chodosh, *Inorg. Chem.*, 1978, **17**, 41-48.