

Secondary Phosphinocarbyne and Phosphaisonitrile Complexes

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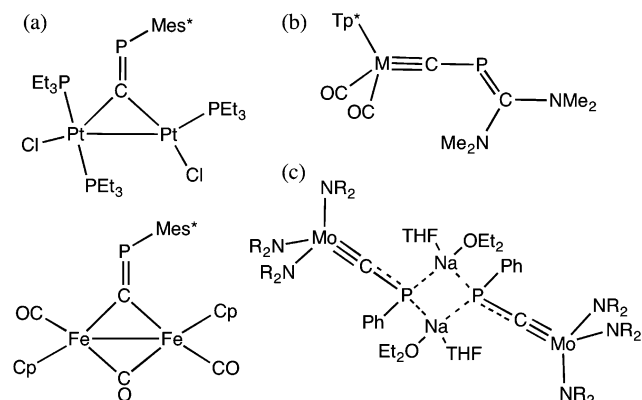
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S Supporting Information

ABSTRACT: The palladium-mediated reaction of $[W(\equiv CBr)(CO)_2(Tp^*)]$ (Tp^* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) with primary phosphines PH_2R ($R = Ph, Cy$) affords the secondary phosphinocarbyne complexes $[W(\equiv CPHR)(CO)_2(Tp^*)]$, deprotonation of which provides the anionic phosphaisonitrile complexes $[W(CPR)(CO)_2(Tp^*)]^-$, including the structurally characterized salt $[W(CPPh)(CO)_2(Tp^*)][K(kryptofix)]$.

Half a century after Wilkinson's serendipitous discovery of the first thiocarbonyl complex $[RhCl(CS)(PPh_3)_2]^{1a}$ and the rich chemistry that followed,^{1b,c} terminal phosphaisonitrile complexes L_nMCPR , the heavier congeners of ubiquitous isonitriles L_nMCNR , remain elusive,² not least because the free molecules CPR are not, to date, isolable. In a similar manner, while cyanide (CN) complexes are commonplace, only two examples of terminal cyaphide (CP) complexes have been isolated.³ Nevertheless, various groups have addressed this challenge and come close to isolating such complexes (Chart 1).⁴⁻⁷

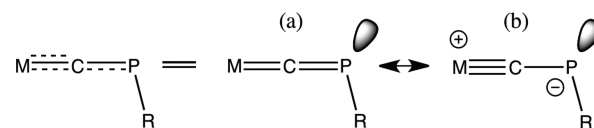
Chart 1. Complexes Relevant to Phosphaisonitrile Coordination Chemistry: (a) Bridging CPR ($Mes^* = C_6H_2tBu_{3-2,4,6}$);^{4,5} (b) Phosphaalkenylcarbyne $CP=CR_2$ ($M = Mo, W$);⁶ (c) Phosphidocarbyne $CPRNa$ ($NR_2 = N^tBuC_6H_3Me_{2-3,5}$)⁷



Three-fragment oxidative addition of thiophosgene is an effective means of installing thiocarbonyl ligands,⁸ leading Angelici to explore similar processes with $Cl_2C=PMes^*$ ($Mes^* = C_6H_2tBu_{3-2,4,6}$),⁴ and while this did indeed afford binuclear phosphaisonitrile-bridged complexes, efforts to convert these to mononuclear species did not meet with success. Further

examples of bridging CPR ligands were provided via nucleophilic attack by, e.g., $PHR(SiMe_3)$ at a bridging thiocarbonyl ligand.⁵ While not phosphaisonitrile complexes per se, Weber's phosphaalkenylcarbyne complexes,^{2,6} which feature a two-coordinate phosphorus carbon substituent, might be described by a valence-bond description that envisages a zwitterionic phosphaisonitrile canonical form. The first and only example of what may be described as a terminal CPR complex was provided by Cummins, who demonstrated the sodium reduction of $[Mo(\equiv CPClPh)(NR_2)_3]$ ($NR_2 = N^tBuC_6H_3Me_{2-3,5}$) to afford $[Mo\{\equiv CPPhNa(OEt_2)(THF)\}(NR_2)_3]_2$.⁷ While clearly incorporating the MoCPPh linkage, the exceedingly π -basic anionic " $Mo(NR_2)_3^-$ " metal center results in substantial transfer of electron density to the phosphorus, such that both structural and computational data (for $[(H_2N)_3MoCPPh]^-$) suggest considerable contribution from a phosphidocarbyne description (Chart 2).

Chart 2. Canonical Forms To Describe L_nMCPR Complexes: (a) Phosphaisonitrile (Phosphaisocyanide); (b) Phosphidocarbyne



Within the chemistry of C_1 ligands, the anionic $Mo(NR_2)_3^-$ fragment falls within the "Schrock-type" regime (coordinatively unsaturated metal center in a high oxidation state coligated by strong (+M) π -donor ligands). With only a single example, the question arises as to whether phosphaisonitrile complexes might be more widely accessible, in particular those adhering to a "Fischer-type" scenario (coordinatively saturated metal center in a low oxidation state coligated by π -acidic ligands), in which more pronounced phosphaisonitrile character might be expected. We report herein a synthetic strategy to construct phosphaisonitrile complexes via deprotonation of the first examples of terminal secondary phosphinocarbyne ligands.

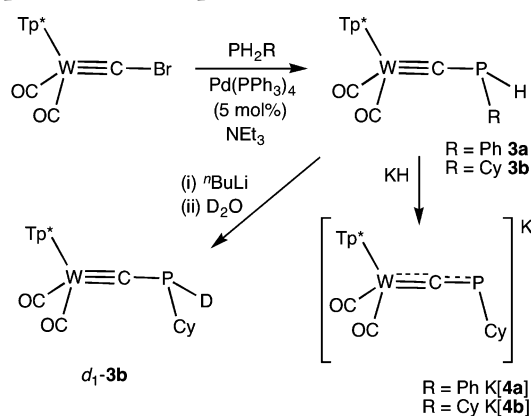
We have previously described the phosphinocarbyne complexes $[M(\equiv CPPh_2)(CO)_2(Tp^*)]$ ($M = Mo$ (**1a**), **W** (**1b**); Tp^* = hydrotris(3,5-dimethylpyrazol-1-yl)borate),⁹ which are conveniently obtained from the reactions of the lithiocarbynes $[M\{\equiv CLi(THF)_x\}(CO)_2(Tp^*)]^{10}$ ($M = Mo$ (**2a**), **W** (**2b**)) with $ClPPh_2$. The metal centers in these complexes are somewhat inert, allowing reactivity studies to focus on the $CPPh_2$ ligand, which in many (though not all)

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respects acts as a conventional phosphine. However, the requisite secondary phosphinocarbyne complexes $[W(\equiv CPHR)(CO)_2(Tp^*)]$ ($R = Ph$ (**3a**), Cy (**3b**)) are not accessible by such a route because secondary chlorophosphines (PHClR) are unavailable, being prone to spontaneous dehydrohalogenation to afford oligomeric *cyclo*-polyphosphines $(PR)_n$. We therefore took a different approach based on our previous demonstration that phosphorus substituents could be installed via palladium-mediated C–P bond formation, as exemplified by the synthesis of $[Mo\{\equiv CP(O)(OEt)_2\}(CO)_2(Tp^*)]$ from $[Mo(\equiv CBr)(CO)_2(Tp^*)]$ and diethyl phosphonate.⁹ Heating a mixture of $[W(\equiv CBr)(CO)_2(Tp^*)]$ and PH_2R ($R = Ph, Cy$) in the presence of $[Pd(PPh_3)_4]$ (5 mol %) and Et_3N provided the new phosphinocarbyne complexes **3a** and **3b**¹¹ in spectroscopically high yields (Scheme 1).¹²

Scheme 1. Synthesis of Secondary Phosphinocarbyne and Phosphaisonitrile Complexes



Spectroscopic data associated with the “ $(Tp^*)(CO)_2W$ ” unit¹¹ conform to copious precedent¹³ and call for little comment other than to note that the chiral secondary phosphine centers in both complexes render the carbonyl ligands diastereotopic (¹³C NMR for **3a**: δ_C 225.6 ($^1J_{WC} = 167.2$ Hz), 225.3 ($^1J_{WC} = 167.6$ Hz)) and the three pyrazolyl environments chemically inequivalent, the implication being that phosphine inversion is slow on the ¹³C NMR time scale. Interest therefore focuses on the CPHR ligand, key data for which include the appearance of a downfield resonance attributable to the carbyne carbon and showing coupling to both phosphorus and tungsten (**3a**: δ_C 289.5 ($^1J_{PC} = 74.2$ Hz, $^1J_{WC} = 187.8$ Hz); **3b**: δ_C 298.3 ($^1J_{PC} = 76.9$ Hz, $^1J_{WC} = 184.1$ Hz)). These data are similar to those observed for **1b** (δ_C 292.6 ($^1J_{PC} = 74.5$ Hz, $^1J_{WC} = 187.9$ Hz))^{9b} and appear in a region typical of more conventional carbynes.¹³ The ³¹P NMR spectra comprise singlet resonances straddled by satellite doublets due to coupling to ¹⁸³W (**3a**: δ_P -12.8 ($^2J_{WP} = 67.3$ Hz); **3b**: δ_P -4.6 ($^2J_{WP} = 64.7$ Hz)), while the ¹H NMR spectra include doublet resonances due to the secondary phosphine proton (**3a**: δ_H 5.81 ($^1J_{PH} = 222.7$ Hz, $^3J_{WH} = 7.8$ Hz); **3b**: δ_H 4.71 ($^1J_{PH} = 210.0$ Hz, $^3J_{HH} = 6.0$ Hz, $^3J_{WH} = 8.4$ Hz)).

The characterization of **3b** included a crystallographic analysis, the results of which are summarized in Figure 1 and may be compared with benchmark data for the complex **1b**.^{9b} The W–C bond lengths for **3b** (1.835(11) Å) and **1b** (1.827(2) Å) are essentially identical, as are the P1–C1 bond lengths (**1b**: 1.783(3) Å; **3b**: 1.785(11) Å), i.e., the disparate steric profiles of the PPH₂ and PHCy substituents do not appear

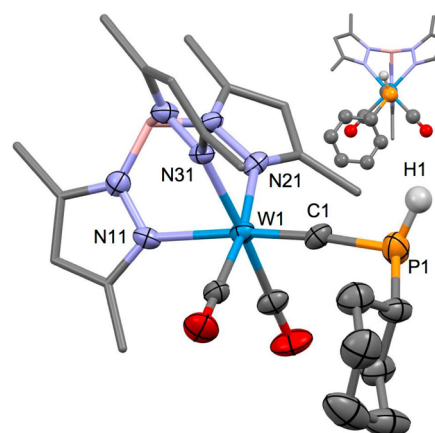


Figure 1. Molecular structure of (*S*)-**3b** in a crystal of *rac*-**3b** (50% displacement ellipsoids, hydrogen atoms except H1 omitted, *R* enantiomer generated by $P21/n$ symmetry, pyrazolyl groups simplified). Inset: View along the P1–C1–W1 spine. Selected bond lengths (Å) and angles (deg.): W1–C1 1.835(11), C1–P1 1.785(11), P1–C41 1.872(11), W1–C1–P1 168.7(7), C1–P1–C41 106.4(5).

to impinge upon the geometry of the W–C–P spine, which in both cases is nearly linear (**1b**: $166.62(15)^\circ$; **3b**: $168.7(7)^\circ$).^{14,15} The adopted conformer places the bulky cyclohexyl substituent distal to the imposing steric encumbrance exerted by the Tp^* ligand.

In anticipation of the generation of a phosphaisonitrile complex, the acidity of the P–H bond of **3b** was investigated. Treating **3b** with an excess of ^tBuLi followed by quenching with D₂O afforded *d*₁-**3b** (C_6D_6 : δ_D -6.2 ($^1J_{PD} = 32.3$ Hz, $\gamma_D/\gamma_H = 0.154$)), though at best 70% deuteration was achieved, even with stronger bases (^tBuLi, ^tBuLi-tmeda). The base of choice was found to be potassium hydride, which, being heterogeneous, could be used in excess. Thus, deprotonation of **3b** with KH in THF afforded solutions of the phosphaisonitrile complex $K[W(CPCy)(CO)_2(Tp^*)]$ (**K[4b]**) that in the strict absence of moisture remained unchanged over 24 h (NMR). For **K[4b]**, the ³¹P signal appears at δ_P 113.9 in benzene-*d*₆, whereas in THF in the presence of dibenzo-18-crown-6 it is observed at δ_P 114.5, i.e., there is little if any ion pairing. This is in contrast to the strong solvent dependence displayed by Cummins' complex $[Mo(\equiv CPhNa)(NR_2)_3(Et_2O)(THF)]_2$ (δ_P 103.5 (THF), 68.8 (C_6D_6), 126.1 (THF + 12-crown-4)).⁷ Infrared ν_{CO} data for **K[4b]** (THF: 1862, 1753 cm^{-1}) may be usefully compared with those for $[Et_4N][Mo(CS)(CO)_2(Tp^*)]$ (1886, 1794 cm^{-1})¹⁶ and $[^nBu_4N][W(CS)(CO)_2(Tp)]$ (1884, 1787 cm^{-1}),¹⁷ which would support the description of **[4b]**[−] as an anionic phosphaisonitrile complex by analogy with thiocarbonyl ligands. Unfortunately, while the salts $Na[W(CN\text{Et})(CO)_2(Tp^*)]$ (1731, 1685, 1649 cm^{-1})¹⁸ and $Na[Mo(CNR)(CO)_2(Tp^*)]$ ($R = Me, ^tBu, Ph$)¹⁹ have been described, the infrared data for the former are uninformative because of apparent ion pairing and data for the latter have not been reported.

Similar results were obtained with **3a** to afford **K[4a]**, for which ¹³C{¹H} data were also acquired. The ¹³C{¹H} NMR spectrum of **K[4a]** showed a significant downfield shift (ca. 70 ppm) for the phosphaisonitrile resonance (THF-*d*₆: δ_C 358.9 ($^1J_{WC} = 183.1$ Hz)) with a particularly large ¹J_{PC} coupling constant (100.6 Hz), consistent with increased P–C multiple bonding (i.e., significant *s* character) in the W–C–P linkage. Unfortunately, the resonance of interest for $[Mo\{\equiv CPhNa\}-$

(OEt₂)(THF)(NR₂)₃]₂ has not been reported. However, we previously observed a similar difference in chemical shift (60 ppm) between the selenolatocarbonyl [Mo(≡CSeMe)(CO)₂(Tp*)] (δ_C 269.3) and the selenocarbonyl complex [Et₄N][Mo(CSe)(CO)₂(Tp*)] (δ_C 328.9).^{10,20} Treating this solution with 1 equiv of iodomethane afforded the phosphinocarbonyl complex [W(≡CPMePh)(CO)₂(Tp*)] (**5**).¹¹

Layering a THF solution of K[**4a**] and 2.2.2-kryptofix with diethyl ether afforded crystals of [K(2.2.2-kryptofix)][**4a**] suitable for diffractometry. The geometry of the anion [**4a**]⁻, which has no intermolecular contacts of note with the cation, is depicted in Figure 2. Relative to the W–C–P spine of **3b**, that

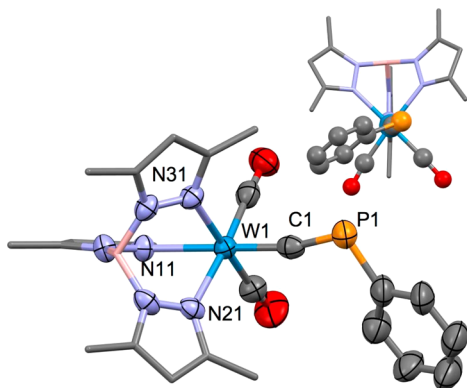


Figure 2. Molecular structure of [**4a**]⁻ in a crystal of [K(2.2.2-kryptofix)][**4a**] (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl groups simplified). Inset: View along the P1–C1–W1 spine. Selected bond lengths (Å) and angles (deg.): W1–C1 1.915(7), C1–P1 1.692(7), P1–C41 1.830(8), W1–C1–P1 167.0(4), C1–P1–C41 104.4(3).

of [**4a**]⁻ reveals some interesting features that further substantiate its formulation as a phosphonitrile complex. Specifically, the W1–C1 bond in [**4a**]⁻ (1.915(7) Å) is elongated relative to that of **3b**, while the C1–P1 bond is contracted (1.692(7) Å; cf. 1.785(11) Å for **3b** and 1.771(5) Å in Cummins' dimer⁷). Similar variations in W–C–P bond lengths were calculated for the hypothetical complexes [W(CPMe)(CO)₅] and [W(≡CPMe₂)(CO)₅]⁺.^{9b} However, the angle at phosphorus (104.4(3)°) is essentially unchanged from that found for **3b** (106.4(5)°).

In conclusion, both spectroscopic and structural data for [**4**]⁻ suggest that there is a considerable contribution from the phosphonitrile valence-bond description (Chart 2a). These complexes, however, clearly lie at the electron-rich end of what will eventually be a metal-dependent spectrum of reactivity as further synthetic routes to phosphonitrile complexes emerge.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, spectroscopic data, and crystallographic data in CIF format for **3b** (CCDC 1032152) and [K(kryptofix)][**4a**] (CCDC 1032151). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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- (11) For experimental procedures and characterization data, see the Supporting Information.
- (12) These syntheses also afford small amounts of the bimetallic bridging carbonyl complexes RP{C≡W(CO)₂(Tp*)}₂, the formation of which may be optimized by varying the reagent stoichiometry. The chemistry of these complexes will be discussed elsewhere. Despite the high yields of **3a** and **3b**, their isolation from the bimetallic carbonyls and PPh₃ required chromatography, which despite being performed at –40 °C still resulted in considerable losses. Accordingly, exploratory work was typically carried out using the crude material, which was typically ca. 88% pure.
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