

Rearrangement of Bis(alkylidynyl)phosphines to Phospha-acyls

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A range of bis(alkylidynyl)phosphines $\text{RP}\{\text{C}\equiv\text{M}(\text{CO})_2(\text{Tp}^*)\}_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Cl}, \text{Ph}, \text{Cy}$; $\text{Tp}^* = \text{hydrotris(dimethylpyrazolyl)borate}$) are obtained from the reactions of $[\text{M}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ with Cl_2PR or alternatively via the palladium(0)-mediated reactions of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ with RPH_2 ($\text{R} = \text{Py}, \text{Cy}$). The complexes $\text{RP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ rearrange slowly ($\text{R} = \text{Cl}$) or on heating ($\text{R} = \text{Ph}$) to afford the isomeric phospha-acyls $[\text{W}_2(\mu\text{-}\eta^1\text{-C};\eta^2\text{-C},\text{P-CCPR})(\text{CO})_4(\text{Tp}^*)_2]$.

The chemistry of iminoacyls (Chart 1) is inextricably linked to that of isonitriles (isocyanides),¹ in that the former generally arise from nucleophilic attack² or migratory insertion processes^{1d,3} involving the latter.

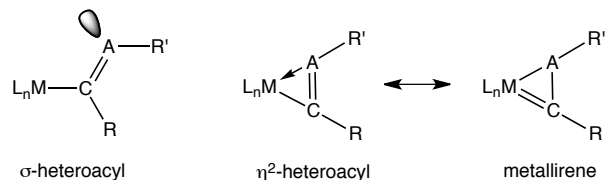
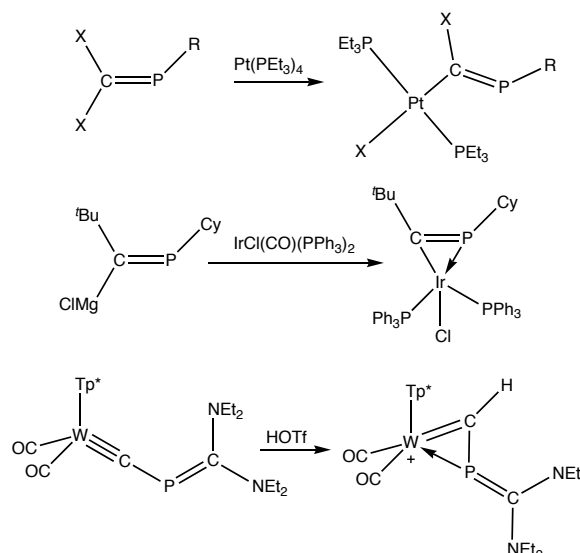


Chart 1. Iminoacyl ($\text{A} = \text{N}$) and Phospha-acyl ($\text{A} = \text{P}$) Complexes.

It is therefore not surprising that a correspondingly rich chemistry of phospha-acyls has yet to emerge, because free phospha-isonitriles (CPR) remain elusive⁴ and their mononuclear complexes are currently limited to $[\text{Mo}(\text{CPhNa}(\text{THF})(\text{Et}_2\text{O}))(\text{N}^t\text{BuC}_6\text{H}_3\text{Me}_2\text{-3,5})_3]$ ⁵ and $[\text{K}(\text{W}(\text{CPR})(\text{CO})_2(\text{Tp}^*))]$ ($\text{R} = \text{Ph}, \text{Cy}$; $\text{Tp}^* = \text{hydrotris(dimethylpyrazolyl)borate}$),⁶ in addition to a small number of binuclear examples.^{7,8} At present, mononuclear phospha-acyl complexes appear limited to two classes (Scheme 1). Angelici has described the oxidative addition of $\text{X}_2\text{C}=\text{PR}$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{N}(\text{SiMe}_3)_2, \text{C}_6\text{H}_2\text{Bu}_3\text{-2,4,6}$) to $[\text{Pt}(\text{PEt}_3)_4]$ to afford $[\text{Pt}(\sigma\text{-C}(\text{X})=\text{PR})\text{X}(\text{PEt}_3)_2]$,⁷ while Jones has described the reaction of Vaska's complex with the phospha-acyl Grignard reagent $\text{CyPC}^t\text{BuMgCl}(\text{OEt}_2)$ to provide an η^2 -phospha-acyl (iridaphosphirene) complex.⁹ Both these approaches in

principle promise some generality, though they have yet to be more widely explored. A third example that might be described as reflecting metallaphosphirene character is Weber's salt $[\text{W}\{\eta^2\text{-HCP}=\text{C}(\text{NEt}_2)_2\}(\text{CO})_2(\text{Tp}^*)]\text{OTf}$.¹⁰



Scheme 1. Installation of Phospha-acyl Ligands.^{7,9,10} $\text{R} = \text{C}_6\text{H}_2\text{Bu}_3\text{-2,4,6}$, $\text{N}(\text{SiMe}_3)_2$.

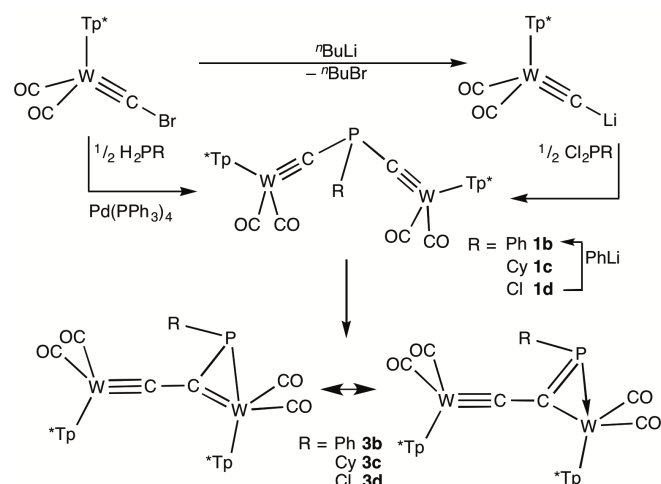
We report herein the isolation of a new class of phospha-acyl complex that arises from an unprecedented rearrangement of bis(alkylidynyl)phosphines that are also without precedent.

Cummins reported the synthesis of the first phosphinocarbyne complexes $[\text{Mo}(\equiv\text{CPRCl})(\text{N}^t\text{BuC}_6\text{H}_3\text{Me}_2\text{-3,5})_3]$ ($\text{R} = \text{Cl}, \text{Ph}$) via the reactions of $[\text{Mo}(\equiv\text{CK})(\text{N}^t\text{BuC}_6\text{H}_3\text{Me}_2\text{-3,5})_3]$ with Cl_2PR .⁵ In a similar manner, the reactions of $[\text{M}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ ¹¹ with ClPPh_2 afford the phosphinocarbynes $[\text{M}(\equiv\text{CPPH}_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo},^{12} \text{W}^{13}$). We therefore considered whether such a strategy might afford access to bimetallic species in which two metals were bridged by a bis(alkylidynyl)phosphine group. The reaction of $[\text{Mo}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ with half an equivalent of Cl_2PPh was investigated and disappointingly found to provide a mixture of two compounds, one of which is the desired bimetallic species $\text{PhP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ (**1a**). The second, a mononuclear

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complex $[\text{Mo}(\equiv\text{C}^n\text{BuPh})(\text{CO})_2(\text{Tp}^*)]$ (**2**), arises from a competing reaction of the presumed intermediate $[\text{Mo}(\equiv\text{CPClPh})(\text{CO})_2(\text{Tp}^*)]$ with adventitious $^n\text{BuLi}$ remaining from the lithium/halogen exchange process by which $[\text{Mo}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ is generated.¹¹ Although full spectroscopic data could be acquired for both complexes **1a** and **2**, they proved inseparable in useful amounts. In the case of tungsten, however, the complex $\text{PhP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ (**1b**) could be obtained in high yield (Scheme 2).



Scheme 2. Synthesis of Bis(alkylidyne)phosphine and Phospha-acyl Complexes.

Alternatively, the conditions and stoichiometry of the palladium-mediated reaction of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ with H_2PR ($\text{R} = \text{Ph}, \text{Cy}$) that previously provided $[\text{W}(\equiv\text{CPR})(\text{CO})_2(\text{Tp}^*)]$,⁶ may be modified to afford $\text{RP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ ($\text{R} = \text{Ph}$ **1b**, Cy **1c**, Scheme 2) in good yields. Spectroscopic data associated with the $(\text{Tp}^*)(\text{CO})_2\text{W}$ units¹⁴ conform to copious precedent for Tp^* ligated carbyne complexes¹⁵ leaving only those associated with the C_2PR spine for comment. The $^{13}\text{C}\{^1\text{H}\}$ NMR signals for the carbyne carbon nuclei (**1a**: 297.6, $^1J_{\text{CP}} = 92$; **1b**: 285.0 ppm, $^1J_{\text{PC}} = 79$, $^1J_{\text{WC}} = 192$; **1c**: 291.1 ppm, $^1J_{\text{PC}} = 80$, $^1J_{\text{WC}} = 190$ Hz) appear in a region similar to that for $[\text{M}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$: 309.0, $^1J_{\text{CP}} = 84$; $\text{M} = \text{W}$: 292.6 $^1J_{\text{PC}} = 75$, $^1J_{\text{WC}} = 188$ Hz)^{12,13} whilst the ^{31}P resonances (**1a**: 80.2; **1b**: 80.4, $^2J_{\text{PW}} = 76$; **1c**: 87.8 ppm, $^2J_{\text{WP}} = 68$ Hz) are to substantially lower frequency of those for the mononuclear diphenylphosphino derivatives ($\text{M} = \text{Mo}$ 35.5; $\text{M} = \text{W}$ 32.0 ppm, $^2J_{\text{WP}} = 69$ Hz). The characterization of **1b** and **1c**¹⁴ included crystallographic analyses, the results of which are summarized in Figure 1.

For carbyne complexes of the form $[\text{M}(\equiv\text{CR})(\text{CO})_2(\text{Tp}^*)]$ ¹⁵ the recurrent geometric features are: (i) A pronounced *trans* influence exerted by the carbyne ligand relative to the two CO ligands; (ii) Angles between the carbyne carbon and adjacent pyrazolyl nitrogens are marginally obtuse while those between the carbyne and carbonyl ligands are slightly acute; (iii) Substantial bending at the carbyne carbon is commonly encountered.¹⁵⁻¹⁷ These are all manifest in the structures adopted by **1b** and **1c**. Focusing on the C_2PR spine, the angle sums at phosphorus (**1b**: 314.7, 316.2; **1c**: 309.9°) and the $\equiv\text{C}-\text{P}$ bond lengths (**1b**: 1.791-1.799, **1c**: 1.784, 1.789 Å) may be compared with those for a simple alkynylphosphine, e.g., $\text{HC}\equiv\text{CPh}_2$ (304.0° and 1.775 Å, respectively),¹⁸ suggesting that

the bonding is entirely conventional, with no indication of noteworthy distortions.

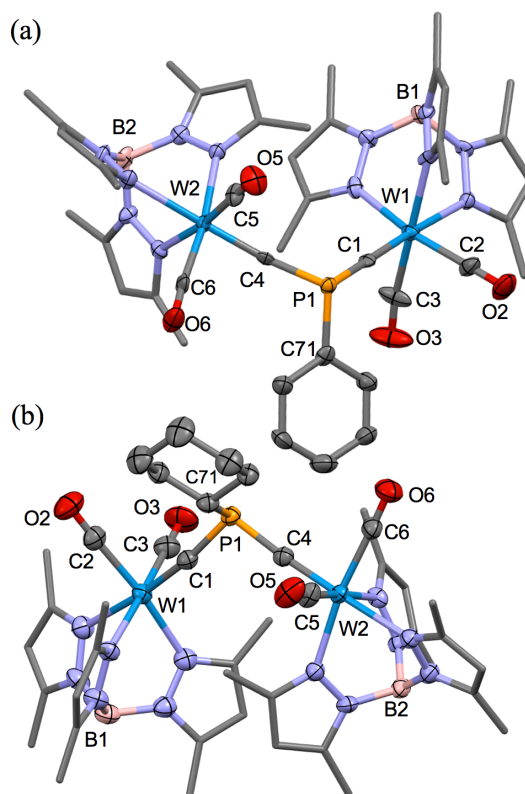


Figure 1. (a) Molecular structures of (a) **1b** in a crystal of **1b**. $(\text{C}_5\text{H}_{12})_{0.25}$ and (b) **1c** in a crystal of **1c**. C_6H_6 (50% displacement ellipsoids, hydrogen atoms and solvate omitted, pyrazolyl groups simplified).

Both the spectroscopic and structural data for **1** point towards these bimetallic complexes being somewhat exotic phosphines and we will report separately on their *P*-based coordination chemistry.¹⁸ An unusual point of departure, however, emerged when we attempted to prepare the analogous complex $\text{ClP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ (**1d**) from $[\text{W}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ and PCl_3 . While **1d** could indeed be observed *in situ* and also converted to **1b** with PhLi , attempts to isolate the **1d** led to mixtures containing a second species shown to be the isomeric phospha-acyl complex $(\mu\text{-ClPCC})\{\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ (**3d**). At room temperature in benzene, the half-life for conversion to **3d** is 7 days and, while the proportion of **3d** could be increased by heating the mixture, neither **1d** nor **3d** survived chromatography and could not be isolated in pure form other than by manual separation of individual crystals (*vide infra*). Nevertheless, limited spectroscopic data could be gleaned from spectra of mixtures (Supporting Information). For **1d** the carbyne resonance appeared at $\delta_{\text{C}} = 280.0$ ($^1J_{\text{PC}} = 98$, $^1J_{\text{WC}} = 194$ Hz), and that for the phosphorus nucleus at $\delta_{\text{P}} = 124.9$ ($^2J_{\text{WP}} = 66$ Hz), to substantially lower frequency *cf.* **1a-c** as expected for replacement of one hydrocarbyl substituent with chloride. On conversion to **3d** this resonance shifted to higher frequency (92.7 ppm) though no coupling to ^{183}W could be discerned. The formulation of **3d** therefore rests on a crystallographic analysis (Figure 2), the results of which will be discussed below together with those for the related complex $(\mu\text{-PhPCC})\{\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$ (**3b**).

With the identity of **3d** established, the thermolysis of **1b** was explored. This complex is indefinitely stable at room temperature (*cf* **1d**) and its conditions of synthesis (80 °C, 18 hours) further attest to its thermal stability. Nevertheless, heating a sample of **1b** in toluene at reflux results in the slow conversion to **3b**. As with the conversion of **1d** to **3d**, the most notable spectroscopic change involves the dramatic shift to higher frequency of the ³¹P resonance from +80.4 to -74.5 ppm and an even higher frequency resonance is observed for **3c** (-111.9 ppm). Inclusion of phosphorus within small rings is typically reflected in upfield ³¹P NMR shifts,¹⁹ *e.g.*, the phosphirenes RPC₂Ph₂ ($\delta_P = -81.5$ R = Cl,²⁰ -190.3 R = Ph²¹). High frequency shifts are also observed for Jones' iridaphosphirene (-157.2)^{9a} and Matthey's binuclear 'W(CO)₅' stabilised tungstaphosphirene [W₂(μ -PhPCPh)(CO)₇(η -C₅H₅)] (-188.7).²² Both **2b** and **2d** were structurally characterized as racemates (*Pca*2₁ and *P2*₁/*c* space groups). Although the latter was less precisely modeled due to systematic twinning in five measured crystals, the geometric features associated with the W₂C₂PR (R = Cl, Ph) unit of interest were similar for both compounds.

The data associated with the alkylidyne component are unremarkable, while those for the phospho-acyl unit have few relevant precedents for comparison. The tungstaphosphirene W1-C1 bonds (**3b**: 2.014(12), **3d**: 1.96(2)Å) are similar in length to those for related acyls,²³ thioacyls²⁴ and selenoacyls²⁵ [M(η^2 -ACR)(CO)₂(L)] (M = Mo, W; A = O, S, Se; L = Tp, Tp*) and iminoacyls of the form [M(η^2 -RCNR')(CO)₂(L)] (L = η -C₅H₅,^{3b} η^5 -C₉H₇,^{26a} κ^3 -Tp^{26b}). Given that these also fall within the range typical of 'Fischer-Type' carbenes, (≥ 2.0 Å) it is appropriate to infer a modest degree of multiple bond character ("metallirene" Fig. 1). The immediate point of distinction however is that for all the structurally characterized iminoacyls, the nitrogen is trigonal, whilst the exocyclic angles at phosphorus for both **3b** (107.7, 109.5°) and **3d** (105.2, 110.2°) are clearly pyramidalized as with isolobal phosphirenes.^{20b,21} Though anti-aromatic 1*H*-azirines have yet to be isolated, geometry optimization (B3LYP-6-311++G**) of 1*H*-trimethylazirine and trimethylphosphirene indicates a pyramidalized pnictogen in *both* cases.

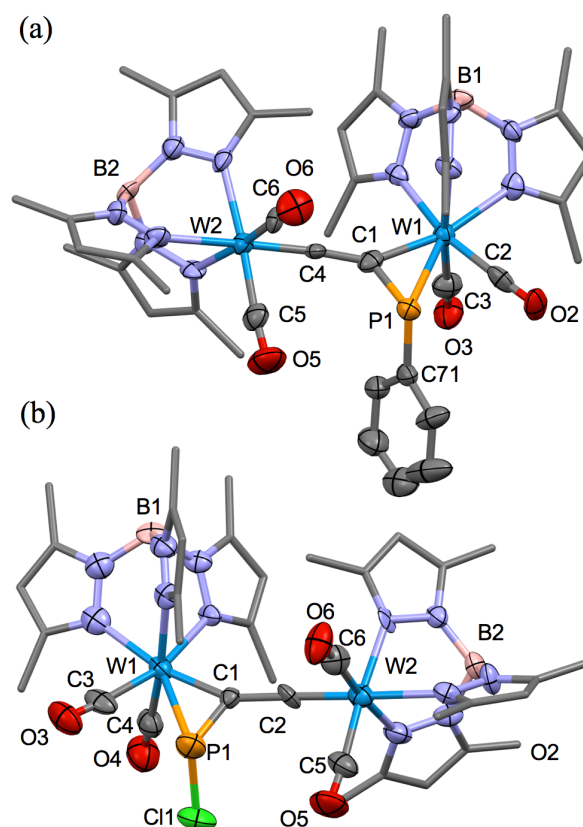


Figure 2. (a) Molecular structure of *R*-**3b** in a crystal of *rac*-**3b**.C₆H₆ (50% displacement ellipsoids, hydrogen atoms and solvate omitted, pyrazolyl groups simplified, *S*-enantiomer generated by *Pca*2₁ symmetry). Selected bond lengths (Å) and angles (deg.): W1-C1 2.014(12), W2-C4 1.865(10), C1-C4 1.380(14), C1-P1 1.790(12), W1-P1 2.585(3), P1-C71 1.821(15), W1-C1-C4 148.1(9), W2-C4-C1 169.2(10), W1-P1-C1 51.0(4), W1-C1-P1 85.4(5), P1-C1-C4 124.5(9), P1-W1-C1 43.7(3), W1-P1-C71 109.6(5), C1-P1-C71 107.8(7). (b) Molecular structure of *R*-**3d** in a crystal of *rac*-**3d**.(CH₂Cl₂)₂ (50% displacement ellipsoids, hydrogen atoms and solvate omitted, pyrazolyl groups simplified *S*-enantiomer generated by *P2*₁/*c* symmetry). Selected bond lengths (Å) and angles (deg.): W1-C1 1.958(19), W2-C2 1.82(2), C1-C2 1.47(3), C1-P1 1.75(2), W1-P1 2.517(7), P1-C11 2.155(12), W1-C1-C2 152.1(16), W2-C2-C1 171.3(17), W1-P1-C1 50.8(7), W1-C1-P1 85.3(9), P1-C1-C2 122.4(15), P1-W1-C1 43.8(6), W1-P1-C11 110.2(4), C1-P1-C11 105.2(8).

We note that the hypothetical and isolobally related rearrangement of propynyldimethylphosphine to 1,2,3-trimethylphosphirene is only mildly endergonic (B3LYP-6-311++G**): $\Delta G = +23.6$ kJmol⁻¹) reflecting a balance between ring strain in the latter and the high energy C=C triple bond of the former. In condensed phases, the observation of such a rearrangement would seem unlikely given that phosphirenes are unstable with respect to dimeric 1,2-dihydro-1,2-diphosphinines.²⁸

The reaction of [Mo(\equiv CBr)(CO)₂(Tp*)] with Li₂S was recently shown to afford the novel thioxoethynylidene bridged complex [Mo₂(μ -CCS)(CO)₄(Tp*)₂] in a reaction presumed to proceed via an intermediate but not observed bis(alkylidynyl)sulfide complex S{C \equiv Mo(\equiv C)(CO)₂(Tp*)}₂ akin to **1**.^{24d} The isolation of complexes **1** and their demonstrated rearrangement to **3** therefore substantiates this mechanistic conjecture though the generality of such rearrangements to other heteroatoms remains to be explored.

We gratefully acknowledge the financial support of the Australian Research Council (DP110101611 and DP130102598).

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