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Tungsten-Platinum μ -Carbido and μ -Methylidyne ComplexesBenjamin J. Frogley^a and Anthony F. Hill^{a*}

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Reactions of the lithiocarbyne $[W]\equiv C\text{Li}$ ($[W] = W(\text{CO})_2(\text{Tp}^*)$; $\text{Tp}^* = \text{tris(dimethylpyrazolyl)borate}$) with divalent platinum complexes $[\text{PtCl}(\text{terpy})]\text{PF}_6$, $[\text{PtCl}_2(\eta\text{-C}_4\text{R}_4)]$ ($\text{R} = \text{Me}, \text{Et}$), and $[\text{PtCl}_2(\text{phen})]$ afford access to μ -carbido, μ -methylidyne and carbyne-based metallo-ligand complexes $[\text{Pt}(\text{C}=[W])(\text{terpy})]\text{PF}_6$, $[\text{Pt}(\mu\text{-HC}=[W])_2]$ and $[\text{Pt}(\text{C}=[W])\text{Cl}(\text{pheny-C}=[W]\text{-}2)]$, respectively, the last of which provides a rare example of intermolecular organometallic nucleophilic attack at coordinated phenanthroline.

Bimetallic μ -carbido bridged complexes L_nMCML_n are rare and intriguing species that may be described by one of three bonding scenarios: (i) Symmetrical 'cumulenonic' bonding between, in most cases, identical metal termini (Class A, Chart 1);¹ (ii) Metallacarbynes in which disparate metals are bound by single and triple metal-carbon bonds (Class B)² and (iii) Polar-covalent (dative, Class C) coordination arising from coordination of a terminal carbido complex, *e.g.*, $[\text{Ru}(\text{C})\text{Cl}_2(\text{PCy}_3)_2]$, to a wide range of late transition metal centres.³ These generally reflect the effective atomic number requirements (1, 2 or 3 valence electrons) of the metal termini.

$\text{L}_n\text{M}=\text{C}=\text{ML}_n$	$\text{L}_n\text{M}\equiv\text{C}-\text{M}'\text{L}_n$	$\text{L}_n\text{M}\equiv\text{C}:\rightarrow\text{M}'\text{L}_n$
Class A dimetallacumulene	Class B metallacarbyne	Class C polar covalent

Chart 1. Three classes of bimetallic μ -carbido complexes.

Binuclear carbido complexes in which one metal is a group 10 element are limited to (i) The unstable tungsten-nickel complex $[\text{W}(\mu\text{-C})\text{Cl}(\text{CO})_2(\text{PEt}_3)_2(\text{Tp}^*)]$ ($\text{Tp}^* = \text{hydrotris(dimethylpyrazolyl)borate}$),^{2f} the spectroscopically characterised complex $[\text{MoPt}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]^{2c}$ and a range of Class C ' $\text{Ru}\equiv\text{C}:\rightarrow\text{ML}_n$ ' complexes that arise from the reactions of $[\text{Ru}(\equiv\text{C})\text{Cl}_2(\text{PCy}_3)_2]$ with unsaturated group 10 reagents.³

Scheme 1. Group 10 μ_2 -carbido complexes. (i) $[\text{NiCl}_2(\text{PEt}_3)_2]$,^{2f} (ii) $[\text{PtCl}_2(\text{COD})]$,⁵ (iii) $[\text{PdCl}_2(\text{SMe}_2)_2]$,^{3a} (iv) $[\text{PtCl}_2(\text{py})_2]$,^{3f} (v) $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{py})]$.^{3b}

Furthermore, the intermediacy of a Class C carbido complex was also implicit in the ultimate formation of a class B metallacarbyne (Scheme 1iv).^{3e}

We have begun to explore the strategic synthesis of group 10 μ -carbido complexes by exploiting the synthetically versatile lithiocarbyne complexes $[\text{M}(\equiv\text{C})\text{Li}](\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$ **1a**, W **1b**),^{2g} given that previous studies with main group electrophiles had provided access to novel carbyne derivatives.⁴ In one case, with $[\text{FeCl}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$, such an approach afforded a Class B molybdenum-iron μ -carbido complex^{2g} that Templeton had previously obtained *via* a complementary strategy.^{2b} Our initial foray did most likely involve a putative ditungsten platinum Class B bis(carbido), $[(\text{COD})\text{Pt}(\text{C}=\text{W}(\text{CO})_2(\text{Tp}^*))_2]$ (**2**, $\text{COD} = 1,5$ -cyclo-octadiene, Scheme 1⁵) from the reaction of **1b** with $[\text{PtCl}_2(\text{COD})]$, however the isolated complex was a 'Pt(COD)' adduct of a ditungstabutadiyne $[\text{W}_2\text{Pt}(\mu\text{-C}_2)(\text{CO})_4(\text{COD})(\text{Tp}^*)_2]$ (**3**)⁵ arising from coupling of two μ -carbido ligands.

We report herein the successful application of the lithiocarbyne transmetalation strategy to afford stable platinum carbido complexes, in addition to two examples of

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CCDC 1945291–1945293 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

situations where the protocol leads to unexpected results, specifically (i) The synthesis of a novel metallocarbyne ligand *via* a rare example of nucleophilic attack at coordinated phenanthroline and (ii) The first example of a bis(methyldiyne) complex.

The reaction of the tungsten lithiocarbyne **1b** (generated *in situ* from $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]]$ and $^n\text{BuLi}$)^{2g} with $[\text{PtCl}(\text{terpy})]\text{PF}_6$ (terpy = 2,2':6',2''-terpyridine) furnishes $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}(\text{Pt}(\text{terpy}))]\text{PF}_6$ (**4**, Scheme 2) as a bright purple solid. The intense low energy absorption ($\lambda_{\text{max}} = 547 \text{ nm}$, $\epsilon = 2510 \text{ Lmol}^{-1}\text{cm}^{-1}$) corresponds to a $d\pi(\text{Pt}) \rightarrow \pi^*(\text{terpy})$ MLCT transition, appearing to slightly higher wavelength of the corresponding absorption for alkynyl analogues $[\text{Pt}(\text{C}\equiv\text{CR})(\text{terpy})]^+$.⁷ This μ -carbido complex adopts the metallocarbyne (Class B) bonding mode, with a formal tungsten–carbon triple bond and platinum–carbon single bond.

Scheme 2. Reactions of a tungsten lithiocarbyne with divalent platinum complexes. (i) $[\text{PtCl}(\text{terpy})]\text{PF}_6$; (ii) $[\text{PtCl}_2(\eta\text{-C}_4\text{R}_4)]$ ($\text{R} = \text{Me}, \text{Et}$); (iii) $[\text{PtCl}_2(\text{phen})]$; $[\text{W}] = \text{W}(\text{CO})_2(\text{Tp}^*)$, mechanistic conjecture in blue.

Acetonitrile was found to be the only conventional solvent in which **4** is sufficiently soluble for useful NMR data to be acquired. In the ^1H NMR spectrum, the Tp^* resonances are found in the usual range and reflect a local C_5 -symmetric environment for the tungsten coordination sphere. The terpyridine proton resonances are noticeably broadened presumably due to the need for the terpy ligand to fit into a cleft provided by two of the adjacent pyrazolyl groups (Figure 1). The $\text{W}\equiv\text{C}(\text{Pt})$ resonance was not located directly in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (presumably due to a combination of the low solubility and coupling to both ^{183}W and ^{195}Pt nuclei) but is tentatively assigned at $\delta_{\text{C}} = 368$ on the basis of ^1H - ^{13}C HMBC correlations with the Tp^* methyl protons. The carbido carbon in

$[(\text{Tp}^*)(\text{CO})_2\text{Mo}\equiv\text{C}(\text{PPh}_3)_2\text{Br}]$, the closest comparator, resonates at 339 ppm.^{2c} The crystal structure of **4** was determined and the molecular geometry of the cation is depicted in Figure 1. The $\text{W}-\text{C}1$ (1.835(5) Å) distance is unremarkable⁶ however, despite the considerable steric encumbrance, the $\text{C}1-\text{Pt}$ bond length (1.938(5) Å) is significantly shorter than found in alkynyl analogues *e.g.*, $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{terpy})]^+$ (1.973(2) Å).⁷ The carbido ligand also exerts a pronounced *trans* influence ($\text{Pt}1-\text{N}8$ 2.002(4) Å) relative to a simple acetylide (1.96–1.98 Å).⁷ The 'Pt(terpy)' plane orients so as to nestle in the cleft provided by two of the pyrazolyl groups to minimize inter-ligand non-bonded interactions (Figure 1 inset) such that restricted rotation about the $\text{W}-\text{C}-\text{Pt}$ axis accounts for the broadening of resonances observed in the ^1H NMR spectrum.

Figure 1. Molecular structure of the cation of **4** (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms and the PF_6^- counteranion omitted for clarity). Selected distances [Å] and angles [°]: $\text{W}1-\text{C}1$ 1.835(5), $\text{C}1-\text{Pt}1$ 1.938(5), $\text{Pt}1-\text{N}7$ 2.013(5), $\text{Pt}1-\text{N}8$ 2.002(4), $\text{Pt}1-\text{N}9$ 2.030(5), $\text{W}1-\text{N}1$ 2.316(4), $\text{W}1-\text{N}3$ 2.226(5), $\text{W}1-\text{N}5$ 2.234(5), $\text{W}-\text{C}1-\text{Pt}$ 176.3(3), $\text{C}1-\text{Pt}-\text{N}7$ 97.4(2), $\text{C}1-\text{Pt}-\text{N}8$ 176.2(2), $\text{C}1-\text{Pt}-\text{N}9$ 102.0(2). Inset = orientation of terpy (pale green) and borate (pink) ligands.

With the proof of concept established, it was envisaged that a similar reaction of **1b** with $[\text{PtCl}_2(\text{phen})]$ (phen = 1,10-phenanthroline) would also provide direct access to a metallocarbyne. Although disubstitution was a possibility (as inferred in the formation of **3**),⁵ the steric bulk of the Tp^* ligand was expected to discourage this and allow isolation of $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{PtCl}(\text{phen})]$ (**6**), retaining a reactive $\text{Pt}-\text{Cl}$ bond for subsequent functionalisation. The reaction provided, however, a major product identified as $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}(\text{Pt}(\text{phen}))]\text{Cl}$ (**5**). (Scheme 2). The complex **5** involves substitution of one chloride to furnish one metallocarbyne $\text{W}\equiv\text{C}-\text{Pt}$ linkage, as anticipated, while a second equivalent of **1b** substitutes at the 2-position to the phenanthroline ligand. The ^1H and ^{13}C NMR spectra contain two sets of Tp^* signals for the independent Tp^* ligands and one set of phenanthroline signals totalling seven protons and twelve carbons. The 'hydrocarbyl' carbyne carbon bound to the phenanthroline ligand resonates at $\delta_{\text{C}} = 267.0$, whereas the dimetallated μ -carbido resonance is located further downfield, at $\delta_{\text{C}} = 331.3$. The structure of **5** has been determined (Figure 2) and, although the low bond precision precludes detailed

interrogation of the geometrical data, it confirms the molecular geometry and position of substitution on the phenanthroline ligand.

Figure 2. Molecular structure of **5** in a crystal of $5 \cdot \text{CHCl}_3$ (50% displacement ellipsoids, pyrazolyl groups simplified and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.853(14), C1–Pt 1.890(14), Pt–N13 2.021(11), Pt–N14 2.154(12), Pt–Cl1 2.289(4), W2–C2 1.868(14), C2–C47 1.42(2), W1–C1–Pt 173.4(9), C1–Pt–N13 91.8(6), C1–Pt–N14 171.5(5), C1–Pt–Cl1 89.6(5), W2–C2–C47 165.3(11).

Free phenanthroline reacts with strongly nucleophilic alkyl and aryl lithiums followed by oxidative re-aromatisation (MnO_2) affording the corresponding 2,9-disubstituted phenanthrolines.⁸ Alkynyl lithiums are, however, insufficiently nucleophilic to participate in such a process (no reaction observed between phen and 10 equiv. $\text{LiC}\equiv\text{CPh}$) and we envisage some parallels in the nucleophilicity of alkynyl lithiums and **1b** for which Templeton has estimated that $pK_a = 28.7$.⁹ Coordination of phenanthroline to a Lewis-acidic transition metal would be expected to enhance its susceptibility towards nucleophilic attack. Despite its ubiquity in coordination chemistry, however, examples of intermolecular nucleophilic attack by organolithium reagents at transition metal coordinated phenanthroline are exceedingly rare, being limited to the reaction of $[\text{Re}(\text{CO})_3(\text{PMe}_3)(\text{phen})]\text{OTf}$ with methyl lithium.¹⁰

Conjecture as to the intimate mechanism for the formation of **5** is equivocal in that whilst the first step almost certainly involves substitution of the first carbyne at platinum to give the μ -carbido $[(\text{Tp}^*)(\text{CO})_2\text{W}=\text{C}-\text{PtCl}(\text{phen})]$ (**6**) as an intermediate, the subsequent introduction of an alkylidynyl substituent onto the phenanthroline ring might take one of two courses. The proposed monocarbido species **6** was not identified or isolable for mechanistic interrogation, even when only one equivalent of **1b** was added to $[\text{PtCl}_2(\text{phen})]$, which implies that subsequent nucleophilic attack by a second equivalent of lithiocarbyne occurs rapidly. Although, as noted above, Pérez has provided the single definitive example of intermolecular attack by an organolithium reagent at a transition metal coordinated phenanthroline ligand,¹⁰ initial attack at the metal was precluded in that instance by the coordinative saturation of the rhenium centre. In contrast, the putative **6** features a d^8 -square planar coordinatively unsaturated metal centre for which nucleophilic attack at the metal is common, although we eschew this route given the pronounced steric clutter around

the platinum centre. The final oxidation step (*cf.* MnO_2 in protocols for free phen functionalisation) presumably occurs upon aerobic work-up and we have been unable to isolate the putative hydrophenanthroline precursor even under anaerobic conditions.

Further attempts to introduce one or two μ -carbido ligands to platinum(II) included the reactions of **1b** with the cyclobutadiene complexes $[\text{PtCl}_2(\eta^4\text{-C}_4\text{R}_4)]$ ($\text{R} = \text{Me}, \text{Et}$)¹¹ in pursuit of ‘half-sandwich’ derivatives of the form $[(\eta^4\text{-C}_4\text{R}_4)\text{Pt}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$, or the reductive elimination isomers, $[\text{W}_2\text{Pt}(\mu\text{-C}_2)(\text{CO})_4(\eta^4\text{-C}_4\text{R}_4)(\text{Tp}^*)_2]$ by analogy with recently reported $[\text{W}_2\text{Pt}(\mu\text{-C}_2)(\text{CO})_4(\eta^4\text{-COD})(\text{Tp}^*)_2]$ (**3**).⁵ Confounding expectations, in both cases ($\text{R} = \text{Me}, \text{Et}$) a single major cyclobutadiene-free orange product was identified as $[\text{W}_2\text{Pt}(\mu\text{-CH})_2(\text{CO})_4(\text{Tp}^*)_2]$ (**7**, Figure 3) in which two parent methylidyne are bridged by a single Pt(0) atom.

Figure 3. Molecular structure of **7** in a crystal of $7 \cdot \text{CH}_3\text{CN}$ showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and most hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.929(8), W2–C2 1.910(8), W1–Pt1 2.7277(4), W2–Pt1 2.7518(5), Pt1–C1 2.046(7), Pt1–C2 2.001(7), Pt1–C4 2.237(7), Pt1–C5 2.319(7), W1–C3 2.012(8), W1–C4 1.962(7), W2–C5 1.970(7), W2–C6 2.002(8), W1–Pt1–W2 166.929(17), C1–Pt1–C2 122.8(3), C1–Pt1–W2 145.4(2), W1–C1–Pt1 86.6(3), W2–C2–Pt1 89.4(3). Inset = W1–C1–Pt1–C4 (red) and W2–C2–Pt1–C5 (blue) planes at 77.7°.

The methylidyne proton gives rise to a singlet resonance at $\delta_{\text{H}} = 12.09$ ($^2J_{\text{HW}} = 44$ Hz) in the ^1H NMR spectrum and the methylidyne carbon nuclei were located at $\delta_{\text{C}} = 293.8$ in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Fluxional interchange of terminal and bridging carbonyl roles occurs at room temperature, but is arrested at -40°C . Although bimetallic μ_2 -methylidyne complexes have attracted sporadic interest^{2b,12,13} very few have been structurally characterised¹³ and all these are homobimetallic. Thus **7** provides the first structural data for a heterobimetallic methylidyne and also the first bis(methylidyne). The trimetallic $\text{W}_2\text{Pt}(\mu\text{-CR})_2$ core motif itself has precedent from the works of Stone on carbyne-assisted metal-metal bond formation,¹⁴ and in the case of **7** inclusion of the sterically protuberant Tp^* and modest methylidyne combination results in insignificant changes to the core geometry (W1–C1 1.929(8), W2–C2 1.910(8), W1–Pt1 2.7277(4), W2–Pt1 2.7518(5) Å) relative to precedent established by $[\text{W}_2\text{Pt}(\mu\text{-CR})_2(\text{CO})_4(\text{L})_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{L} = \eta\text{-C}_5\text{H}_5$; $\text{R} = \text{CH}_3$, $\text{L} = \text{HB}(\text{pz})_3$).¹⁴

The mechanism of formation for **7** invites speculation although the isolation of traces (<5%) of the ditungstabutadiyne $[\text{W}_2(\mu\text{-C}_2)(\text{CO})_4(\text{Tp}^*)_2]$ (**8**)⁵ does suggest its reductive

elimination from the desired bis(carbido) complex. However, consistent with the basicity and steric bulk of **1b**, more competitive would appear to be the E_2 reductive dihydrohalogenation of the platinum complex to afford zerovalent platinum and presumably labile dimethyldimethylene cyclobutene ($R = \text{Me}$).¹⁵ The reaction of isolated $[\text{W}(\equiv\text{CH})(\text{CO})_2(\text{Tp}^*)]$ with $[\text{Pt}(\text{nbe})_3]$ ($\text{nbe} = \text{norbornene}$) was also found to provide **7** although the synthetic sequence is less concise, such that the formation from $[\text{PtCl}_2(\eta^4\text{-C}_4\text{R}_4)]$ remains the preferred synthetic route.

In conclusion, while we have demonstrated that halide metathesis by lithiocarbynes such as **1b** does indeed provide a viable route to Class B platinum carbido derivatives, the uncharted reactivity profile of carbido complexes in general continues to promise many surprises.

Acknowledgements

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

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