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Stoichiometric and Catalytic Demercuration of Bis(tricarbido)mercurials: The First Dimetallaoctatetraynes

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Summary: Treating the complexes $[Hg\{C{\equiv}CC{\equiv}W(CO)_2L\}_2]$ *(L = HB(pz)*$_3$ *(**1a**), HB(pz′)*$_3$ *(**1b**); pz = pyrazol-1-yl; pz′ = 3,5-dimethylpyrazol-1-yl) with 1 equiv of cis-*$[PtCl_2(PPh_3)_2]$ *or a catalytic amount of trans-*$[RhCl(CO)(PPh_3)_2]$ *provides the bimetallic complexes* $[L(CO)_2W{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}W(CO)_2L]$ *(L = HB(pz)*$_3$ *(**2a**), HB(pz′)*$_3$ *(**2b**)), the first examples of dimetallaoctatetra-1,3,5,7-ynes. Catalytic amounts of* $[RhCl(CO)(PPh_3)_2]$ *also provide **2a** and **2b** in good yields.*

Bimetallic complexes spanned by carbon-only ligands have attracted enormous interest in recent years, with the vast majority involving dimetalated polyynes.[1] Thus, there exists an underrepresentation of both odd-numbered carbon-only ligands ($MC_{2y+1}M$) and metal−carbon multiply bonded species ($M{=}C_n{=}M$ and $M{\equiv}C_n{\equiv}M$). We have recently addressed the former problem by developing a number of new routes to bi- and trimetallic tricarbido complexes, $\{W{\equiv}CC{\equiv}C\}_xML'_n$ (x = 1, 2).[2] A small number of dinuclear tricarbido complexes had been discovered by Gladysz[3] and Templeton,[4] prior to our studies. However, our approach afforded unprecedented generality with respect to the choice of metal termini, including the bis(tricarbido)mercurials $[Hg\{C{\equiv}CC{\equiv}W(CO)_2L\}_2]$ (L = HB(pz)$_3$ (**1a**), HB(pz′)$_3$ (**1b**); pz = pyrazol-1-yl, pz′ = 3,5-dimethylpyrazol-1-yl).[2d] Bis(alkynyl)mercurials find utility as trans-alkynylating agents for the synthesis of transition-metal[5−10] and lanthanoid alkynyls;[11,12] however, we have also identified a range of transition-metal complexes that will catalytically extrude the mercury from $[Hg(C{\equiv}CR)_2]$ to provide 1,3-diynes ($RC{\equiv}CC{\equiv}CR$),[13,14] providing a mild alternative to the harsher Glaser−Eglington ($[Cu(OAc)_2]$/hot pyridine) or Hay (CuCl/tmeda/O_2)[15] conditions for alkyne coupling, obviating the need for base or oxidant to be present.

Attempts to extend our silylpropargylidyne-desilylation protocol to the synthesis of tricarbido derivatives of platinum(II) have so far not met with success. However, Cross has previously shown that bis(alkynyl)mercurials serve to deliver either one or two alkynyl groups to platinum(II).[10] In view of this, we have investigated the reactions of **1** with *cis*-$[PtCl_2(PPh_3)_2]$. Stirring **1a** with 1 equiv of the platinum complex *cis*-$[PtCl_2(PPh_3)_2]$ at room temperature for 1 h effected a slow color change from red to deep green. Subsequent chromatography provided a green microcrystalline solid (**2a**). Surprisingly, the same green compound was obtained from the reaction of **1a** with the complex *trans*-$[RhCl(CO)(PPh_3)_2]$, one of the complexes previously shown to effect demercuration of bis(alkynyl)mercurials.[14] Similarly, the compound **1b** with *trans*-$[RhCl(CO)(PPh_3)_2]$ provided the green compound **2b** (Scheme 1). In concert with the reactions between *trans*-$[RhCl(CO)(PPh_3)_2]$ and bis(alkynyl)mercurials,[13] the synthesis of **2** from *either* rhodium or platinum reagents and the spectroscopic data obtained,[21] these are formulated as

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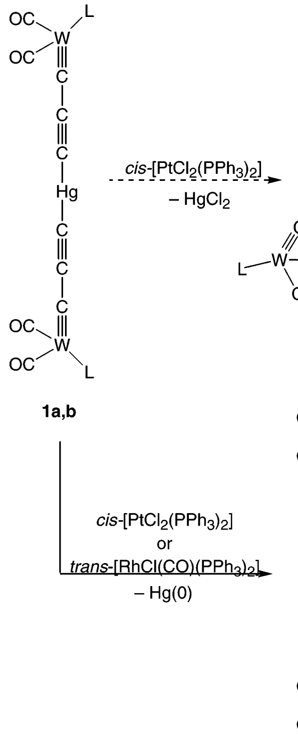
Scheme 1. Synthesis of Hexacarbido Complexes[a]



[a] L = {HB(pz)$_3$} (**a**), {HB(pz′)$_3$} (**b**).

Chart 1. Hexacarbido Valence Bond Forms: (a) Hexatriyndiyl; (b) Cumulenic; (c) Dimetallaoctatetrayne

(a)
$M{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}M$

(b)
$M{=}C{=}C{=}C{=}C{=}C{=}C{=}M$

(c)
$M{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}M$

the coupled C_6 complexes [L(CO)$_2$W≡CC≡CC≡CC≡W(CO)$_2$L] (L = HB(pz)$_3$ (**2a**), HB(pz′)$_3$ (**2b**)). While hexacarbido linked bimetallics were previously known,[16–20] these all contained the polyyne-diyl valence localization ($L_nM{-}C{\equiv}CC{\equiv}CC{\equiv}C{-}ML_n$), while cumulenic $L_nM{=}C{=}C{=}C{=}C{=}C{=}C{=}ML_n$ and bis(alkylidyne) $L_nM{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}ML_n$ forms (Chart 1) were unknown.

The ^{1}H NMR data for **2b** showed little deviation from those of **1b**; however, the ^{13}C NMR signals for the C_6 carbon backbone proved diagnostic. We have found previously[2] that the ^{13}C NMR signals for C_β and C_γ nuclei of the dimetalated tricarbido derivatives [W(≡$C_\alpha C_\beta$≡$C_\gamma ML_n$)(CO)$_2$L] (L = HB(pz)$_3$, HB(pz′)$_3$) are typically shifted to lower field than those of their organyl counterparts [W(≡$C_\alpha C_\beta$≡C_γCMe$_3$)(CO)$_2$L].[22] The resonances for the complex **2b** are found to much higher field (δ 96.2 (C_β), 58.6 (C_γ)) than, for example, the corresponding mercurial complex **1a** (δ 120.5 (C_β), 106.4 (C_γ)). The alkylidyne carbon nuclei (C_α) are, however, comparatively insensitive to changes in substitution at C_γ. The results of a crystal structure determination[21c] of a tris(toluene) solvate of **2b** are summarized in Figure 1, which confirms the WC_6W connectivity and pseudooctahedral geometry at tungsten. A crystallographic inversion center bisects the essentially linear[23] WC_6W spine of the centrosymmetric complex. The bond lengths along the WC_6W chain clearly conform to a localized dimetallaoctatetrayne W≡CC≡CC≡CC≡W valence bond description with W−C1 (1.862(3) Å), C1−C2 (1.342(5) Å), C2−C3 (1.237(5) Å), and C3−C3′ (1.344(7) Å)

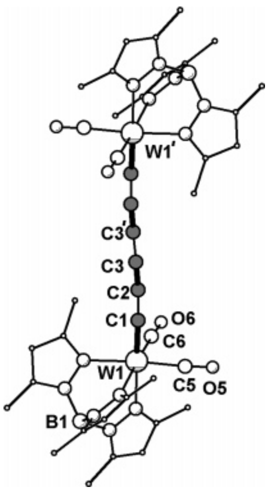


Figure 1. Molecular structure of the complex **2b** (pyrazolyl groups simplified). Selected bond distances (Å) and angles (deg): W1−N11 = 2.260(3), W1−N21 = 2.218(3), W1−N31 = 2.190(3), W1−C1 = 1.862(3), C1−C2 = 1.342(5), C2−C3 = 1.237(5), C3−C3′ = 1.344(7); N11−W1−C1 = 175.91(12), W1−C1−C2 = 175.6(3), C1−C2−C3 = 175.1(4), C2−C3−C3^i = 179.0(5).

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(21) (a) Synthesis of **2a**: **1a** (50 mg, 0.042 mmol), [Bu$_4$N]Cl (7 mg, 0.042 mmol), and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (34 mg, 0.042 mmol) were stirred in CH$_2$Cl$_2$ (5 mL) for 1 h and then freed of volatiles. The residue was chromatographed (silica gel, 1/1 CH$_2$Cl$_2$/petroleum ether), and the green eluate was freed of volatiles to provide a green powder. Yield: 8 mg (19%). IR (Nujol): 1979 vs, 1916 w, 1891 s cm^{-1}. IR (CH$_2$Cl$_2$): 1982 vs, 1915 s, 1890 s cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.96 (d, 4 H, $^3J_{HH}$ = 2.1 Hz, H^3(pz)), 7.66 (d, 4 H, $^3J_{HH}$ = 2.4 Hz, H^5(pz)), 7.57 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, H^3(pz)), 7.52 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, H^5(pz)), 6.27 (t, 4 H, $^3J_{HH}$ = 2.1 Hz, H^4(pz)), 6.12 (t, 2 H, $^3J_{HH}$ = 2.1 Hz, H^4(pz)). Useful ^{13}C NMR data could not be obtained due to poor solubility. MS (ESI): *m/z* (%) 979 (9) [M]$^+$. N.B: a halide source was used ([Bu$_4$N]Cl) on the (untested) assumption that, as in the case of simple bis(alkynyl)mercurials, nucleophile-induced symmetrization of the resulting [ClHgC≡CR] to [Hg(C≡CR)$_2$] and [HgCl$_3$]$^-$ increases the atom efficiency with respect to “C≡CR” transfer. (b) Synthesis of **2b**: **1b** (50 mg, 0.037 mmol) and [RhCl(CO)(PPh$_3$)$_2$] (3 mg, 4 μmol, 12 mol %) in thf (5 mL) were stirred for 3 h, and the mixture was then freed of volatiles. The residue was chromatographed (silica gel, 40/60 CH$_2$Cl$_2$/petroleum ether) and the green eluate freed of volatiles to provide a deep green powder. Yield: 29 mg (68%). IR (Nujol): 1991 m, 1974 vs, 1904 vs, 1883 m cm^{-1}. IR (CH$_2$Cl$_2$): 1993 m, 1975 vs, 1901 vs cm^{-1}. ^{1}H NMR (25 °C, CDCl$_3$): δ 5.97 (s, 4 H, H^4(pz′)), 5.78 (s, 2 H, H^4(pz′)), 2.51 (6 H), 2.40 (6 H), 2.32 (3 H), 2.31(3 H) (s × 4, CH$_3$(pz′)). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 242.8 (C≡W), 227.4 (W−CO), 152.1 (1 C), 151.9 (2 C) (C^5(pz)), 145.5 (1 C), 144.8 (2 C) (C^3(pz)), 106.3 (1 C), 106.2 (2 C) (C^4(pz)), 96.2 (W≡C*C*≡C), 58.6 (W≡CC≡*C*), 15.8 (2 C), 14.5 (1 C) (C^{3}Me(pz)), 12.0 (1 C), 11.9 (2 C) (C^{5}Me(pz)). MS (ESI): *m/z* (%) 1159 (10) [M − CO + MeCN]$^+$, 1146 (25) [M]$^+$, 1118 (3) [M − CO]$^+$. Anal. Found: C, 42.13; H, 4.05; N, 14.22. Calcd. for $C_{40}H_{44}B_2N_{12}O_4W_2$: C, 41.92; H, 3.87; N, 14.66. (c) Crystal data for **2b**·3C$_7$H$_8$: $C_{40}H_{44}B_2N_{12}O_4W_2\cdot 3C_7H_8$, M_r = 1422.61, monoclinic, $P2_1/n$, a = 11.6309(1) Å, b = 20.1331(3) Å, c = 13.7340(1) Å, β = 104.9562(7)°, V = 3107.09(6) Å^3, Z = 2, ρ_{calcd} = 1.520 g cm^{-3}, μ(Mo Kα) = 3.754 mm^{-1}, T = 200 K, green plate, 7108 independent measured reflections ($2\theta \leq 55°$), R1 = 0.0219, wR2 = 0.0259 for 4734 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 360 parameters. CCDC 264360.

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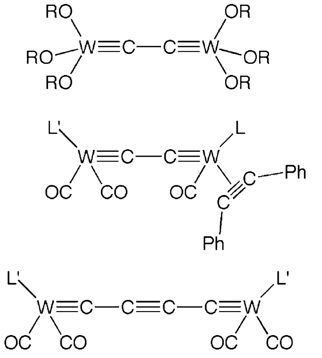
(23) One indication of deviation from net linearity is given by the sum of bond lengths along the chain: cf. the distance between metals. In the case of **2a** this is within the limits of experimental uncertainty (0.020(33) Å).

Chart 2. Bimetallic Complexes with Carbon-Only Bis(alkylidyne) Ligands[a]



[a] Tp = {HB(pz)$_3$}; Tp′ = {HB(pz′)$_3$}; R = ^{t}Bu.

separations falling within norms for W≡C, C≡C, and C−C bond lengths, respectively. This is in clear contrast to structural data for hexatriynediyl complexes.[16−18] The hexacarbido ligand also exerts the typical trans influence observed for more conventional alkylidyne ligands in the tris(pyrazolyl)borate complexes $[W(\equiv CR)(CO)_2L]$.[24]

Bimetallic complexes with carbon-only bis(alkylidyne) ligands are potentially interesting in terms of electronic communication along the carbon chain. Their alkylidyne functionality, being much more π-acidic than σ-alkynyl M−C(*sp*) single bonds, should facilitate better communication between the two metal centers given a greater participation of the metal π-orbitals in bonding with the carbon chain. This might be expected to reduce the energy of any MLCT absorptions (relative to polyynediyls) which underpin electrooptical applications for dimetalated polycarbyls. Despite this potential, only three examples (Chart 2) have been reported to date by Schrock[25] and Templeton,[26,27] based on bis(alkylidyne) C_2 or C_4 linkages. The question arises as to whether the hexacarbido linkage is in any way distinct from more conventional alkylidyne linkages, a question the complex **2b** is well placed to address, given the diversity of known alkylidyne complexes of the form $[W(\equiv CR)(CO)_2\{HB(pz')_3\}]$ for comparison. Table 1 provides infrared (k_{CO}) and ^{13}C NMR (δ_{WC}) data for a selection of such complexes,[2d,27−33] indicating very little change in either parameter within the "alkynyl" substituted series of alkylidyne derivatives. However, Figure 2, which depicts the UV/vis spectra for **1a**, **2a**, and the simple propargylidyne $[W(\equiv CC\equiv CSiMe_3)(CO)_2\{HB(pz')_3\}]$ (**3b**),[33] clearly shows behavior for the hexacarbido complex **2a** that is distinct from that of **1a** or **3b**. The low-energy band we attribute to the alkylidyne MLCT absorption (λ^1) is of comparable wavelength and molar extinction for both **1b** and **3b** but is shifted to higher wavelength for **2b** with higher extinction. A similar trend is

Table 1. Selected Spectroscopic Data for Alkylidyne Complexes[a]

complex	IR k_{CO}	^{13}C NMR $\delta(M\equiv C)$	vis λ^1_{max} (ϵ')	UV λ^2_{max} (ϵ')
$[W]\equiv CH$[28]	15.20[b]	280.6		
$[W]\equiv CCH_3$[29]	15.01[c]	289.3[d]		
$[W]\equiv CC_6H_4Me$-4[30]	15.06[e]	279.6		
$[W]\equiv CNEt_2$[31]	14.35	248.6		
$[W]\equiv COMe$[32]	14.74[b]	228.2		
$[W]\equiv CC\equiv CSiMe_3$[33]	15.19[b]	247.3[d]	510 (305)	275 (5790)
$\{[W]\equiv CC_2\}_2Hg$[2d]	15.19	246.7[d]	516 (645)	312 (4195)
$[W]\equiv CC_2C\equiv[W]$[27]	15.09[c]	243.7[d]		
$[W]\equiv CC_4C\equiv[W]$	15.14	242.8	645 (1040)	395 (11 100)

[a] [W] = $W(CO)_2\{HB(pz')_3\}$. Unless otherwise noted, data are reported from CH_2Cl_2 or CD_2Cl_2. $k_{CO} = (2.0191 \times 10^{-6}\ N\ m^{-1})(\nu_1^2 + \nu_2^2)$; ϵ' values (L mol^{-1} cm^{-1}) are corrected for complex nuclearity, i.e., the molar extinction coefficient $\epsilon = \epsilon'$(W nuclearity). [b] THF. [c] KBr. [d] $CDCl_3$. [e] Hexane.

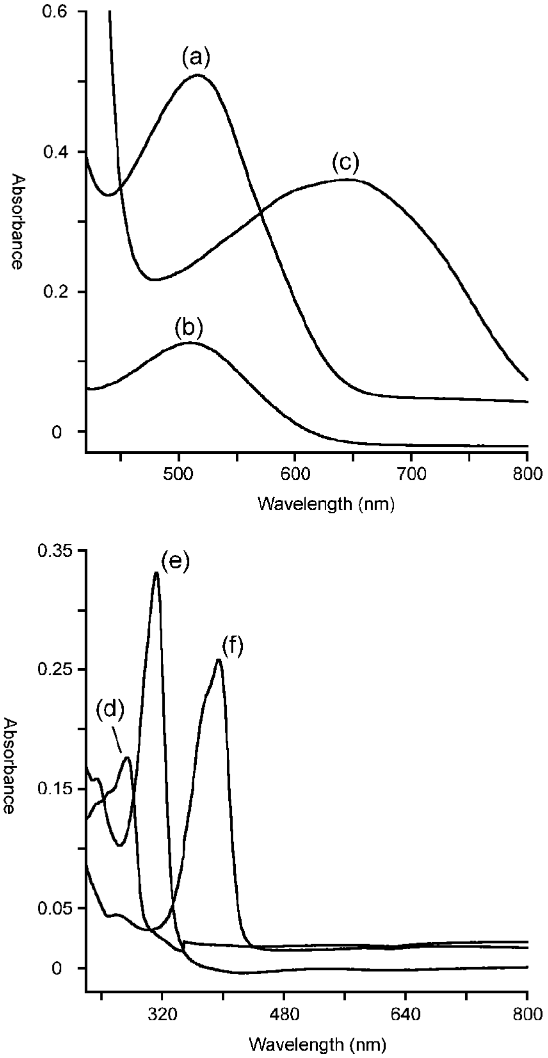


Figure 2. UV−visible spectra of complexes **1b**−**3b**: (a) **1b** (7.89 mmol L^{-1}); (b) **3b** (8.32 mmol L^{-1}); (c) **2b** (3.46 mmol L^{-1}); (d) **3b** (0.059 mmol L^{-1}); (e) **1b** (0.079 mmol L^{-1}); (f) **2b** (0.024 mmol L^{-1}).

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observed for λ^2, which we presume is due to CO-associated MLCT transitions. The behavior of λ^1 is consistent with (i) the hexacarbido linkage in **2b** displaying extended electronic delocalization in the excited state and (ii) the $d^{10}s^0$ Hg^{II} center in **1b** serving as an effective electronic insulator.

Given that rhodium is lost in the synthesis of complexes **2**, presumably as regenerated $[RhCl(CO)(PPh_3)_2]$, the possibility that it would serve in a catalytic capacity was investigated. Under ambient conditions, 10 mol % of the rhodium complex was sufficient to smoothly catalyze the conversion of **1b** to **2b** (nonoptimized). Furthermore, it was established that the prior isolation of **1b** was not necessary but, rather, that it could be generated in situ (from $HgCl_2$, **3b**, and $[Bu_4N]F$), making the complex **2b** readily accessible on a large scale for our ongoing studies. We expect that the mechanism of catalysis is analogous to that which we have proposed for simple bis(alkynyl)mercurials; however, the formation of **2b** from **1b** and $[PtCl_2(PPh_3)_2]$ must proceed via a different mechanism that first involves transalkynylation in a manner akin to that described by Cross for the reactions of platinum chloro complexes with simple bis(alkynyl)mercurials.[10]

Supporting Information Available: Full details of the crystal structure determination of **2b**·$3C_6H_5Me$ (CCDC 264360), including tables giving positional and thermal parameters and a figure giving an ORTEP representation. This material is available free of charge via the Internet at http://pubs.acs.org.

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