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Reactions of Bis(tricarbido)mercurials and Dimetallaoctatetraynes with $[Ru(CO)_2(PPh_3)_3]$: Scission of a $C_{sp}-C_{sp}$ Single Bond

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Summary: The reactions of $[L(CO)_2WC_6W(CO)_2L]$ *(L =* $HB(pz)_3$*,* $HB(pz')_3$*; pz = pyrazol-1-yl, pz′ = dimethylpyrazol-1-yl) with* $[Ru(CO)_2(PPh_3)_3]$ *provide the bis(tricarbido) complexes* $[(Ph_3P)_2(CO)_2Ru\{C_3W(CO)_2L\}_2]$ *via the adduct* $[(Ph_3P)_2(CO)_2Ru\{\eta^2\text{-}L(CO)_2WC_6W(CO)_2L\}]$*, which, along with* $[(Ph_3P)_2(CO)_2Ru\{C_3W(CO)_2L\}\{HgC_3W(CO)_2L\}]$*, is observed as an intermediate in the reactions of* $[Ru(CO)_2(PPh_3)_3]$ *with* $[Hg\{C_3W(CO)_2L\}_2]$ *that also ultimately provide the bis(carbido) complex.*

There has in recent times been an enormous effort directed toward the synthesis of long-chain dimetalated poly-ynes, $L_nM-(C{\equiv}C)_x-(C{\equiv}C)_y-ML_n$.[1] Many of the synthetic protocols involve the coupling of smaller-chain monometalated building blocks, $L_nM-(C{\equiv}C)_{x,y}-R$ (R = H, $SiMe_3$, Li, MgBr, halide, etc.), by extension of conventional alkynyl coupling procedures. Thus the formation of $C_{sp}-C_{sp}$ single bonds between two (poly)alkynyl groups has underpinned progress in this field. Our interest in heterobimetallics spanned by the tricarbido linkage[2] has led us to add the catalytic demercuration of bis(polycarbyl)mercurials to the armory of applicable alkynyl coupling protocols. This was demonstrated with the demercuration of the bis(tricarbido)mercurials $[Hg\{C_3W(CO)_2L\}_2]$ (L = $HB(pz)_3$ **1a**, $HB(pz')_3$ **1b**; pz = pyrazol-1-yl, pz′ = 3,5-dimethylpyrazol-1yl),[2d] which could be catalyzed by $[RhCl(CO)(PPh_3)_2]$ to provide the first examples of dimetallaoctatetraynes $[L(CO)_2W{\equiv}C-C{\equiv}C-C{\equiv}C-C{\equiv}W(CO)_2L]$ (L = $HB(pz)_3$ **2a**, $HB(pz')_3$ **2b**).[3] The mechanism we envisage for this process naturally follows that previously proposed for the catalytic demercuration of bis(alkynyl)mercurials by $[RhCl(CO)(PPh_3)_2]$ and the salt $[Rh(PPh_3)_2([9]aneS_3)]PF_6$ (Scheme 1).[4] Thus we presume addition of one Hg−C bond (**A** → **B**) is followed by extrusion of elemental mercury to provide a *cis*-bis(alkynyl) rhodium(III) intermediate (**B** → **C**) that readily reductively eliminates the diynyl group (**C** → **D**). Given the centrality of oxidative addition and reductive elimination steps to this sequence, we have now turned our attention to the fragment “$Ru(CO)_2(PPh_3)_2$”,[5] which is formally isoelectronic with $[RhCl(CO)(PPh_3)_2]$. By replacing a $d^8\text{-}L_4Rh^I$ center with one based on $d^8\text{-}L_4Ru^0$ we anticipated that oxidative addition ($Ru^0 \rightarrow Ru^{II}$) would be more facile, while reductive elimination would be less favored, thereby possibly allowing us to intercept mechanistically

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[5] The complex $[Ru(CO)_2(PPh_3)_3]$ is synthetically equivalent to “$Ru(CO)_2(PPh_3)_2$” by virtue of facile phosphine dissociation in solution: Cavit, B. E.; Grundy, K. R.; Roper, W. R. *Chem. Commun.* **1972**, 60.

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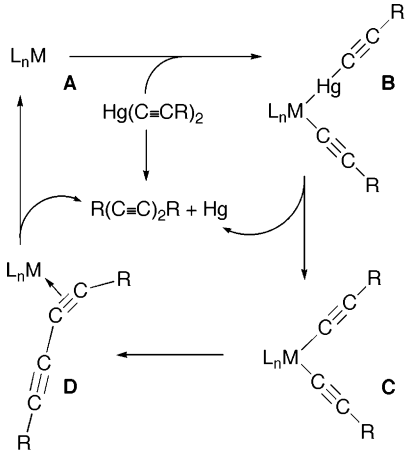
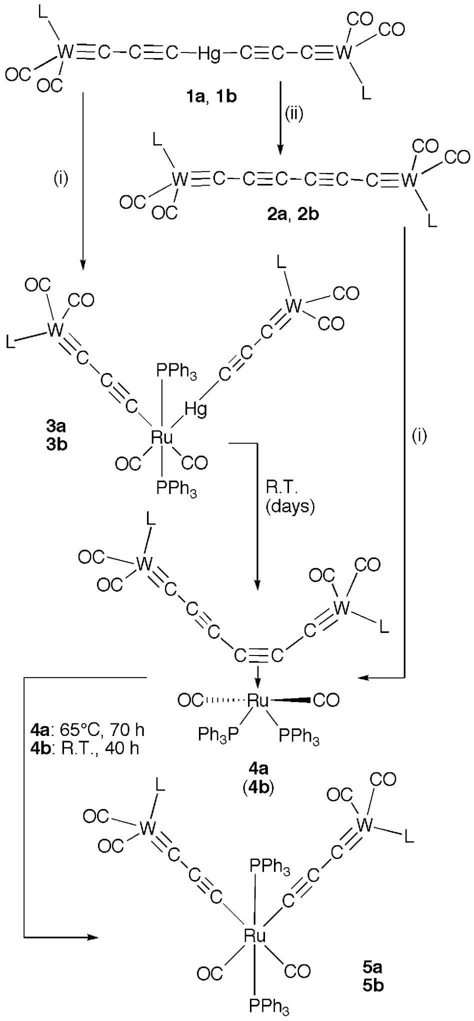
Scheme 1. Proposed Mechanism for the Catalytic Demercuration of Bis(alkynyl)mercurials[4]



Scheme 2. Reactions of $[Ru(CO)_2(PPh_3)_3]$ with 1 and 2[a]



[a] '**a**' series L = $HB(pz)_3$, '**b**' series L = $HB(pz')_3$. (i) $[Ru(CO)_2(PPh_3)_3]$; (ii) $[RhCl(CO)(PPh_3)_2]$.

informative intermediates. To preempt the following, this strategy has proven successful in allowing the isolation of intermediates (Scheme 2) analogous to those merely inferred in the rhodium chemistry. However, more remarkably, it transpires that the reverse of the ultimate step, i.e., the scission of a $C_{sp}-C_{sp}$ single bond (**D** → **C**), could be demonstrated for the first time in a mononuclear complex.[6-8]

The reaction of the mercurials **1a** or **1b** with $[Ru(CO)_2(PPh_3)_3]$[5] proceeded at room temperature to provide brown and orange solids, respectively. On the basis of spectroscopic data,[9] these compounds were formulated as $[(PPh_3)_2(CO)_2Ru\{C_3W(CO)_2L\}\{HgC_3W(CO)_2L\}]$ (L = $HB(pz)_3$ **3a**, $HB(pz')_3$ **3b**). Complex **3a** is unstable at room temperature and decomposes over the course of hours; however **3b** was stable. Both solids had multiple absorption bands attributable to the tungsten-bound

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[6] The cleavage of butadiynes has been observed within group 4 metallocene chemistry to provide binuclear bis(μ-alkynyl) derivatives.[7] The cleavage of the $C_{sp}-C_{sp}$ single bond of diynes has been implicated in one process catalyzed by $[Ru_3(CO)_{12}]$;[8a] however by far the more common cleavage of alkynes by polynuclear systems involves the C≡C bond to provide one or two μ-alkylidyne ligands.[8b]

[7] Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V., *Organometallics* **1994**, *13*, 2903.

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[9] Data for complexes: **3a**: $[Ru(CO)_2(PPh_3)_3]$ (72 mg, 0.076 mmol) and **1a** (100 mg, 0.085 mmol) were stirred in THF (5 mL) for 2 h and then filtered through kieselguhr. The filtrate was diluted with ethanol (5 mL) and then slowly concentrated to provide a brown solid, which was filtered off and washed with ethanol and petroleum ether. Removal of volatiles from the filtrate and recrystallization of the residue from CH_2Cl_2 and EtOH provided a second crop. Yield: 95 mg (67%). IR Nujol: 2027, 1974, 1941, 1867sh cm^{-1}. CH_2Cl_2: 2031, 1979, 1946, 1890, 1871 cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.96, 7.86, 7.71, 7.64, 7.43 [m × 5, 42 H, $H^{3,5}(pz) + C_6H_5$], 6.27, 6.17 [m × 2, 6 H, $H^4(pz)$] ppm. $^{31}P\{^1H\}$ NMR: δ 33.7 [s + d, $^2J_{HgP}$ = 382 Hz] ppm. $^{13}C\{^1H\}$ NMR, MS, and analytical data not obtained due to instability. **3b**: $[Ru(CO)_2(PPh_3)_3]$ (70 mg, 0.074 mmol) and **1b** (100 mg, 0.074 mmol) were treated as for the synthesis of **3a** above. Yield: 102 mg (68%). IR Nujol: 2025 $\nu_{C{\equiv}C}$, 1966 (br), 1876, 1861 ν_{WCO}, 1939 ν_{RuCO} cm^{-1}. CH_2Cl_2: 2031 $\nu_{C{\equiv}C}$, 1985, 1970, 1879, 1865 ν_{WCO}, 1942 ν_{RuCO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 7.98 [m, 12 H, $C^{3,5}(C_6H_5)$], 7.15 [t, 12 H, $C^{2,6}(C_6H_5)$], 7.05 [t, 6 H, $C^4(C_6H_5)$], 5.64 (2 H), 5.56 (2 H), 5.37 (1 H), 5.33 (1 H) [s × 4, $H^4(pz)$], 2.78 (6 H), 2.54 (3 H), 2.52 (6 H), 2.45 (3 H) [s × 4, 3-$CH_3(pz)$], 2.14 (6 H), 2.12 (6 H), 2.06 (3 H), 2.03 (3 H) [s × 4, 5-$CH_3(pz)$] ppm. $^{13}C\{^1H\}$ NMR: δ 253.9, 253.6 [W≡C], 227.8, 227.2 [WCO], 201.5, 200.7 [RuCO], 152.6 (2 C), 152.5 (2 C), 152.3 (1 C), 152.1 (1 C) [$C^5(pz)$], 144.5 (1 C), 144.3 (1 C), 143.8 (2 C), 143.5 (2 C) [$C^3(pz)$], 137.0 [vt, J_{PC} = 24.0 Hz, $C^1(C_6H_5)$], 133.7 [$C^{2,6}(C_6H_5)$], 130.5 [$C^4(C_6H_5)$], 129.0 [$C^{3,5}(C_6H_5)$], 106.8 (1 C), 106.7 (2 C), 106.5 (3 C) [$C^4(pz)$], 17.3 (2 C), 16.9 (2 C), 15.5 (1 C), 15.3 (1 C) [3-$CH_3(pz)$], 12.5 (3 C), 12.4 (3 C) [5-$CH_3(pz)$] ppm. $^{31}P\{^1H\}$ NMR: δ 34.3 [s + d, $^2J_{HgP}$ = 360 Hz] ppm. MS (HR ESI): *m/z* 2031.3384 (2) $[M + H]^+$ (calcd 2031.3362). Anal. Found: C, 47.34; H, 4.03; N, 8.10. Calcd for $C_{78}H_{74}B_2HgN_{12}O_6P_2RuW_2{\cdot}C_5H_{12}$(NMR): C, 47.46; H, 4.13; N, 8.00. **4a**: $[Ru(CO)_2(PPh_3)_3]$ (43 mg, 0.046 mmol) and **2a** (50 mg, 0.051 mmol) were stirred in THF (20 mL) for 1 h. Volatiles were removed and the residue crystallized from CH_2Cl_2 and EtOH and dried in vacuo. Yield: 45 mg (59%). IR Nujol: 2061 $\nu_{C{\equiv}C}$, 1998, 1871 (br) ν_{WCO}, 1944 (sh) ν_{RuCO} cm^{-1}. CH_2Cl_2: 1998, 1876 (br) ν_{WCO}, 1945sh ν_{RuCO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 7.93−7.05 [m, 42 H, $C_6H_5 + H^{3,5}(pz)$], 5.89 (2 H), 5.75 (2 H), 5.60 (1 H), 5.59 (1 H) [s × 4, $H^4(pz)$] ppm. $^{13}C\{^1H\}$: δ 300.3 [$W{\equiv}\mathit{C}C_2Ru$], 253.4 [$W{\equiv}\mathit{C}C{\equiv}CC_2Ru$], 230.1, 229.0 [WCO], 205.3 [RuCO], 146.1 (2 C), 145.4 (2 C), 144.2 (1 C), 143.9 (1 C) [$C^5(pz)$], 135.2 (2 C), 134.6 (2 C) [$C^3(pz)$], 135.0 [$C^{2,6}(C_6H_5)$], 133.4 [vt, J_{PC} = 22.7 Hz, $C^1(C_6H_5)$], 130.3 [$C^4(C_6H_5)$], 128.8 [$C^{3,5}(C_6H_5)$], 120.9 [$W{\equiv}C-\mathit{C}{\equiv}C-C_2Ru$], 77.0 [$W{\equiv}C-C{\equiv}\mathit{C}-C_2Ru$] ppm. Two $C^3(pz)$ signals could not be identified due to poor signal/noise ratio. $^{31}P\{^1H\}$ NMR: δ 46.3 ppm. MS (ESI): *m/z* 1659 (<1) $[M]^+$. Anal. Found: C, 46.95: H, 3.03; N, 9.97. Calcd for $C_{66}H_{50}B_2N_{12}O_6P_2RuW_2{\cdot}0.5CH_2Cl_2$ (NMR): C 46.93, H 3.02, N 9.88. **5b**: $[Ru(CO)_2(PPh_3)_3]$ (49 mg, 0.052 mmol) and **2b** (50 mg, 0.044 mmol) were stirred in CH_2Cl_2 (5 mL) for 18 h. The mixture was filtered through Celite and diluted with hexane. Slow concentration provided a brown solid, which was filtered off and recrystallized from CH_2Cl_2/hexane. Yield: 30 mg (37%). IR Nujol: 2058 $\nu_{C{\equiv}C}$, 2000, 1863 ν_{WCO}, 1944 ν_{RuCO} cm^{-1}. CH_2Cl_2: 2063 $\nu_{C{\equiv}C}$, 2003, 1867 ν_{WCO}, 1947 ν_{RuCO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.01, 7.41 [m × 2, 30 H, C_6H_5], 5.82 (4 H), 5.75 (2 H) [s × 2, $H^4(pz)$], 2.36 (6 H), 2.35 (12 H) [s × 2, 3-$CH_3(pz)$], 2.30 (6 H), 2.15 (12 H) [s × 2, 5-$CH_3(pz)$] ppm. $^{13}C\{^1H\}$: δ 254.8 [W≡C], 226.9 [WCO], 192.2 [RuCO], 152.6 (2 C), 152.4 (1 C) [$C^5(pz)$], 145.4 (1 C), 144.8 (2 C) [$C^3(pz)$], 134.5 [$C^{2,6}(C_6H_5)$], 134.2 [vt, J_{PC} = 25.0 Hz, $C^1(C_6H_5)$], 130.6 [$C^4(C_6H_5)$], 128.5 [$C^{3,5}(C_6H_5)$], 106.5 (1 C), 106.4 (2 C) [$C^4(pz)$], 16.6 (2 C), 15.2 (1 C) [3-$CH_3(pz)$], 12.7 (3 C) [5-$CH_3(pz)$] ppm. $^{31}P\{^1H\}$ NMR: δ 23.5 ppm. MS (ESI): *m/z* 1866 (9) $[M - 6(CO) + 5(MeCN)]^+$, 1828 (100) $[M]^+$, 1607 (15) $[M - PPh_3 + MeCN]^+$, 1566 (37) $[M - PPh_3]^+$. Anal. Found: C, 51.60; H, 4.41; N, 8.90. Calcd for $C_{78}H_{74}B_2N_{12}O_6P_2RuW_2$: C 51.25, H 4.08, N 9.20.

carbonyls, and each showed two different environments in their ^{1}H NMR spectrum for the ligands "L". Complexes **3a** and **3b** displayed singlet resonances in their ^{31}P{^{1}H} NMR spectra (δ_P 33.7 and 34.3, respectively), overlaid with doublets due to ^{199}Hg−^{31}P coupling ($^{2}J_{HgP}$ = 382 and 360 Hz, respectively). Although the instability of **3a** precluded acquisition of satisfactory ^{13}C{^{1}H} NMR data, the ^{13}C{^{1}H} spectrum of **3b** further confirmed the inequivalence of the two "$C_3W(CO)_2\{HB(pz)_3\}$" moieties. Two signals were found for each of the W−CO, Ru−CO, and W≡C$_\alpha$ nuclei, the signals of each pair being separated by less than 1 ppm. High-resolution ESI mass spectrometry confirmed the empirical formula of **3b**.

The penultimate mechanistic candidate in the proposed rhodium manifold would be a labile diyne adduct (**D**, Scheme 1). In contrast to [RhCl(CO)(PPh$_3$)$_2$], the "Ru(CO)$_2$(PPh$_3$)$_2$" fragment is known to form stable alkyne and diyne adducts [Ru(η^2-PhC≡CR)(CO)$_2$(PPh$_3$)$_2$] (R = Ph,[10] C≡CPh[11]), while the complex [Ru(η^2-RC≡CR)(CO)$_2$(PPh$_3$)$_2$] (R = 4,7,10-trithiatridecadiyne) has been implicated as a reaction intermediate.[12] The reaction of the dimetallaoctatetrayne **2a** with [Ru(CO)$_2$(PPh$_3$)$_3$] provided a green product assumed to be the π-"alkyne" complex [(PPh$_3$)$_2$(CO)$_2$Ru{η^2-C$_6$(W(CO)$_2${HB(pz)$_3$})$_2$}], **4a**. The infrared spectrum of **4a** was consistent with this formulation, displaying two highly broadened (i.e., unresolved) absorption bands corresponding to the W(CO)$_2$ groups (1998, 1876 cm^{-1}) and one band with a shoulder (1944 cm^{-1}) corresponding to the Ru(CO)$_2$ unit. The ^{31}P{^{1}H} NMR spectrum of **4a** showed one singlet resonance (δ_P 46.3), comparable to those for the analogous PhC$_2$Ph (δ_P 42.5)[10] and PhC$_4$Ph (δ_P 43.8)[11] adducts. The ^{1}H and ^{13}C{^{1}H} NMR spectra showed the expected doubling of signals corresponding to the two distinct HB(pz)$_3$ ligands. The two alkylidyne carbon resonances were identified at δ_C 300.3 and 253.4, the former attributed to that adjacent to the π-bonded carbons. Weak signals were found at δ_C 120.9 and 77.0, tentatively assigned to the noncoordinated alkyne nuclei. However, only one resonance could be located for the Ru(CO)$_2$ carbon nuclei (δ_C 205.3). Given that the structurally characterized PhC$_2$Ph (1963, 1875)[10] and PhC$_4$Ph (1978, 1917)[11] adducts give rise to two carbonyl infrared absorptions while **4a** appears to have only one associated with ruthenium, we suggest that the geometry at ruthenium might involve an approximately *trans*-Ru(CO)$_2$ arrangement with *cis*-equatorial phosphines. This geometry is uncommon for complexes of the form [RuL(CO)$_2$(PPh$_3$)$_2$]; however it has been observed for the maleic anhydride and C$_2$F$_4$ adducts, with the preference being attributed to strong π-acidity of the alkenes.[13] In the case of **4a** it seems more likely that the preference is steric in origin.

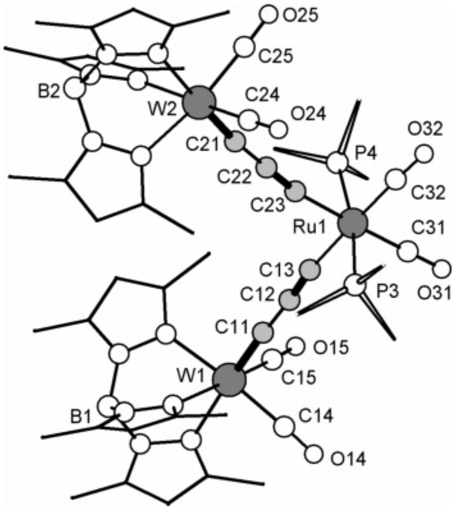

Figure 1. Molecular geometry of **5b** in a crystal of **5b**·(C$_6$H$_6$)$_{4.5}$ (pyrazolyl groups simplified, phenyl groups and hydrogen atoms omited). Selected bond distances (Å) and angles (deg): W1−C11 1.867(11), W2−C21 1.836(11), Ru1−C13 2.057(11), Ru1−C23 2.059(12), C11−C12 1.358(14), C12−C13 1.236(14), C21−C22 1.357(14), C22−C23 1.234(14), P3−Ru1−P4 171.4(1), C13−Ru1−C23 96.7(5), C13−Ru1−C31 84.7(6), C23−Ru1−C32 86.5(5), C31−Ru1−C32 92.1(6), W1−C11−C12 176.9(9), C11−C12−C13 174.0(11), Ru1−C13−C12 171.6(10), W2−C21−C22 173.2(9), C21−C22−C23 179.6(10), Ru1−C23−C22 169.7(9).

Storage of complex **3a** (δ_P 33.7) at room temperature also results in the formation of **4a** as one of the major decomposition products. Heating a sample of **4a** (65 °C, 70 h) results in the clean formation of a new product formulated as the bis(tricarbido) complex [Ru(CO)$_2$(PPh$_3$)$_2$(C$_3$W(CO)$_2${HB(pz)$_3$})$_2$] (**5a**) by virtue of its ^{31}P{^{1}H} NMR spectrum (δ_P 26.1); no other phosphorus-containing species were observed. In a similar manner, heating **3b** (δ 34.3) resulted in the formation of a mixture of products, which included a significant proportion of the bis(tricarbido) derivative **5b** (δ_P 23.5) but none of the π-adduct **4b**. From this we presume that the steric factors that lead to the unexpected stereochemistry of **4a** are sufficiently exaggerated in "**4b**" that it does not persist in solution,[14] but rather proceeds spontaneously to the oxidative addition product, **5b**. In support of this interpretation, the reaction of [Ru(CO)$_2$(PPh$_3$)$_3$] with **2b** also provides **5b**, without the presumed intermediate **4b** being observed. The spectroscopic data for **5b** indicate only a single HB(pz′)$_3$ environment. The ^{31}P{^{1}H} NMR spectrum comprised one resonance substantially shifted from that of the π-complex **4a**. The ^{13}C{^{1}H} NMR spectrum showed only single resonances for the RuCO, WCO, and alkylidyne carbon nuclei (δ_C 192.2, 226.9, and 254.8, respectively), their positions in keeping with those seen for the RuC$_3$W tricarbido complexes previously reported.[2a] The complex **5b** was thus formulated as a bis(tricarbido) RuW$_2$ complex, *trans,cis,cis*-[(PPh$_3$)$_2$(CO)$_2$Ru(C$_3$W(CO)$_2${HB(pz′)$_3$})$_2$] (**5b**), a formulation that was confirmed crystallographically for a benzene solvate. The results of this study[15] are summarized in Figure 1. The crystal structure possesses pseudosymmetry elements that compromise the precision of the structural model refinement and deter detailed interpretation of geometrical parameters. The

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(13) Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Ware, D. C. *J. Organomet. Chem.* **1990**, *398*, 133.

(14) Phosphorus-31 NMR spectra of some preparations of **5b** included a minor resonance at δ_P = 41.2, which would be consistent with the presence of the postulated π-adduct **4b**; however this was never isolated in pure form.

requisite nonroutine modeling procedures are outlined in the Supporting Information. Nevertheless, the connectivity and topology of the molecule followed unequivocally. Averaged values for the two crystallographically independent tricarbido arms fall within norms for tricarbido "MC_3W" complexes.[2] The geometry at ruthenium is essentially pseudooctahedral, although it involves a significant splaying of the WC_3RuC_3W spine (W−Ru−W 109.14(2)°).

Metal-mediated C≡C bond activations of alkynes have been well-studied, primarily in cluster complexes,[8b] while metathesis of the multiple bond is fundamental to alkyne dismutation. However, cleavage of the single $C_{sp}-C_{sp}$ single bond of di- or poly-ynes by monometallic centers is we believe unprecedented. With recourse to the different redox properties and coordination number preferences of isoelectronic d^8-Ru^0 and d^8-Rh^I centers, we have identified model complexes for intermediates in the catalytic demercuration of bis(tricarbido)mercurials, and by extrapolation, bis(alkynyl)mercurials in general. However, while these models could be identified, it would appear that the sequence of their evolution is in fact not as initially proposed. Thus the key step, extrusion of mercury from an alkynylmercurio ligand, does not appear to initially provide a σ-alkynyl, but rather a diyne adduct, which either dissociates the diyne (Rh) or ultimately oxidatively adds (Ru) to give a bis(alkynyl). This raises questions as to the nature of the transition state for mercury extrusion; if indeed alkynyl transfer occurs directly to an adjacent alkynyl ligand (four-membered cyclic RuHgCC transition state), then secondary orbital interactions might assist in the case of alkynyls. In this respect we note that the complex $[Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2]$, akin to **3**, is by way of contrast, thermally stable.[16]

Supporting Information Available: Full details of the crystal structure determinations of **5b**·$(C_6H_6)_{4.5}$ (CCDC 273882) including positional and thermal parameters and an ORTEP representation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for **5b**·$(C_6H_6)_{4.5}$: $C_{78}H_{74}B_2N_{12}O_6P_2RuW_2\cdot(C_6H_6)_{4.5}$, $M = 2179.29$, orthorhombic, $Fdd2$, $a = 32.1991(7)$, $b = 45.2295(9)$, $c = 27.0746(5)$ Å, $V = 39430.1(14)$ Å^3, $Z = 16$, $r_{calc} = 1.469$ g cm^{-3}, μ(Mo Kα) = 2.572 mm^{-1}, $T = 200(2)$ K, orange plate, 22 562 independent measured reflections ($2\theta \leq 55°$), $R_1 = 0.073$, $wR_2 = 0.112$ for 16 223 independent observed absorption-corrected reflections [$I > 3\sigma(I)$], 372 parameters. The average intensities of reflections with $h + k + l = 4n$, $4n + 2$, and $4n \pm 1$, respectively, were in the ratio 1000:168:69, which can be rationalized by describing the crystal structure as a displacive modulation away from an idealized $Z = 2$ parent structure with space group $Imm2$ and all axial lengths halved compared to the unit cell of the $Fdd2$ structure. Satisfactory refinement was obtained for each of these sets of reflections. The possibility of stacking faults was considered. The nonroutine procedures for the solution and refinement of the structural model are discussed in detail in the CIF file and Supporting Information. CCDC 273882.

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