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A Bis(tricarbido) Complex of Iridium and Tungsten: $[IrH(C{\equiv}CC{\equiv}W(CO)_2\{HB(pz)_3\})_2(CO)(PPh_3)_2]$

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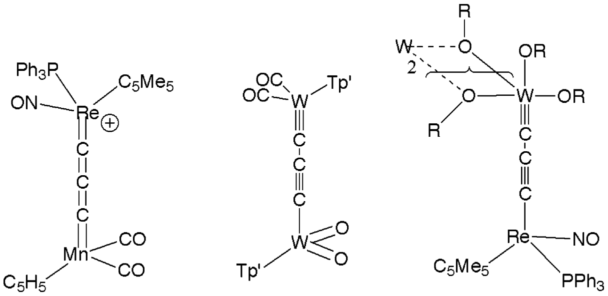
Summary: The fluoride-mediated protodesilylation of $[W({\equiv}CC{\equiv}CSiMe_3)(CO)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) in the presence of Vaska's complex provides the first bis(tricarbido) trimetallic complex, $[IrH(C{\equiv}CC{\equiv}W(CO)_2\{HB(pz)_3\})_2(CO)(PPh_3)_2]$, the crystal structure of which reveals a linear nine-membered WC_3IrC_3W chain.

There is considerable current interest in the synthesis and properties of bimetallic complexes spanned solely by linear carbon chains.[1] Because the most commonly employed reagents in the synthesis of such complexes are polyynyl silanes, phosphines, or terminal polyynes, the vast majority of such complexes involve even-numbered carbon chains, $L_nM{-}(C{\equiv}C)_x{-}ML_n$. Notable exceptions to this are the tricarbido complexes (Chart 1) reported by Gladysz[2,3] and Templeton.[4] Thus, (i) employing the lithiated alkynyl complex $[Re(C{\equiv}CLi)(NO)(PPh_3)(\eta\text{-}C_5Me_5)]$ in a Fischer-type carbyne synthesis with $[Mn(CO)_3(\eta\text{-}C_5H_nCl_{5-n})]$ ($n = 0, 4, 5$) provides the salts $[Re\{C_3Mn(CO)_2(\eta\text{-}C_5H_nCl_{5-n})\}(NO)(PPh_3)(\eta\text{-}C_5Me_5)]BF_4$,[2] (ii) deprotonation of the complex $H_2C[C{\equiv}W(CO)_2\{HB(pzMe_2)_3\}]_2$ ($pzMe_2$ = 3,5-dimethylpyrazol-1-yl) followed by aerial oxidation provides the bimetallic complex $\{HB(pzMe_2)_3\}(OC)_2W{\equiv}CC{\equiv}CW(O)_2\{HB(pzMe_2)_3\}$],[4] and (iii) metathesis of the diynyl ligand in $[Re(C{\equiv}CC{\equiv}CR)(NO)(PPh_3)(\eta\text{-}C_5Me_5)]$ (R = H, Me) by $[W_2(OCMe_3)_6]$*(W≡W)* provides the complex $[Re\{C{\equiv}CC{\equiv}W(OCMe_3)_3\}(NO)(PPh_3)(\eta\text{-}C_5Me_5)]_2$.[3]

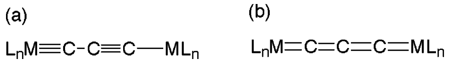
These elegant synthetic strategies established the tricarbido ligand as a viable linker for bimetallic systems, as well as raised a dichotomy regarding the localization of bonding (Chart 2). However, these routes are particular to the systems involved, and accordingly, we have sought a more general approach to tricarbido-linked bimetallics. One such strategy that we have recently reported[5] involves the fluoride-mediated protodesilylation of silylated propargylidyne complexes to generate in situ either $L_nM{\equiv}CC{\equiv}CH$ or its conjugate base. Propargylidyne complexes of tungsten and molybdenum are readily available via a Mayr-type alkylidyne synthesis,[6] and Fischer has recently extended this protocol to obtain silylated examples.[7] Herein we wish to report the extension of our desilylation protocol to iridium, which provides for the first time a trimetallic complex in which the three metal centers are linked by two tricarbido bridges.

Chart 1. Tricarbido Complexes[a]



[a] Tp′ = $HB(pzMe_2)_3$.

Chart 2. Canonical Forms for Tricarbido Complexes: (a) Metallabutadiynyl; (b) 1,5-Dimetallapentatetraene



The complex $[Ir(C{\equiv}CPh)(CO)(PPh_3)_2]$ arises from the reaction of $[Ir(NCMe)(CO)(PPh_3)_2]ClO_4$ with ethynylbenzene under basic conditions.[8] Accordingly, we assumed that treating $[IrCl(CO)(PPh_3)_2]$ with the complex $[W({\equiv}CC{\equiv}CSiMe_3)(CO)_2\{HB(pz)_3\}]$ (pz = pyrazol-1-yl) and $[Bu_4N]F$ would lead to a tricarbido analogue of Vaska's complex, viz. $[\{HB(pz)_3\}(CO)_2W{\equiv}CC{\equiv}C{-}Ir(CO)(PPh_3)_2]$. Spectroscopic and analytical data for the product[9] of this reaction were, however, not consistent with this formulation. Notably, the carbonyl-associated infrared absorption assigned to the iridium carbonyl appeared at a frequency too high for iridium(I) (Nujol: 2017 vs 1955 cm^{-1} for $[Ir(C{\equiv}CPh)(CO)(PPh_3)_2]$[8]). The product was too insoluble for useful $^{13}C\{^1H\}$ NMR data to be acquired; however, the ^1H NMR spectrum indicated the presence of a hydride ligand (δ −8.78), the resonance for which showed coupling to two phosphorus nuclei with a magnitude typical of a *mer,trans*-IrP_2H

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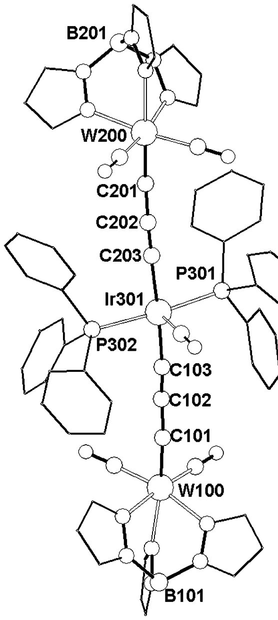
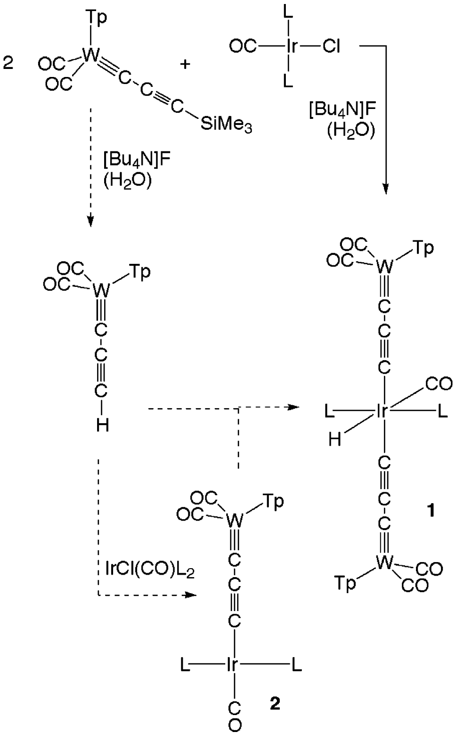


Figure 1. Molecular structure of the complex **1** (phenyl and pyrazolyl groups simplified). Selected bond distances (Å) and angles (deg): Ir301−C103 = 2.042(9), Ir301−C203 = 2.044(9), Ir301−C301 = 2.021(15), W100−C101 = 1.852(11), W100−C104 = 1.968(16), W100−C105 = 1.979(14), W200−C201 = 1.859(10), W200−C204 = 1.966(10), W200−C205 = 1.983(10), C101−C102 = 1.384(15), C102−C103 = 1.192(13), C201−C202 = 1.374(13), C202−C203 = 1.185(12); C103−Ir301−C203 = 172.4(4), W100−C101−C102 = 175.2(8), C101−C102−C103 = 176.8(11), Ir301−C103−C102 = 175.7(9), W200−C201−C202 = 175.3(8), C201−C202−C203 = 178.2(10), Ir301−C203−C202 = 178.1(8).

arrangement ($^2J_{PH}$ = 13.7 Hz). Furthermore, integration of pz and Ph resonances indicated an Ir:W ratio of 1:2, suggesting that the product was the iridium(III) complex [IrH(C≡CC≡W(CO)$_2${HB(pz)$_3$})$_2$(CO)(PPh$_3$)$_2$] (**1**). The identity of the product **1** was confirmed crystallographically, and the results of this study[9] are summarized in Figure 1.

The molecular structure of **1** in the crystal involves pseudo-octahedrally coordinated tungsten and iridium centers, although the iridium hydride ligand was not reliably located. There are no crystallographic elements of symmetry associated with the molecule, and hence, each {HB(pz)$_3$}(CO)$_2$W≡CC≡C "metallo-ligand" is distinct. Nevertheless, corresponding distances within the halves of the WC$_3$IrC$_3$W wire are statistically equivalent and correspond to a localized metallabutadiynyl W≡CC≡C−Ir valence bond description with typical separations for W≡C (1.852(11), 1.859(10) Å), ≡CC≡ (1.384(15), 1.374(13) Å), C≡C (1.192(13), 1.185(12) Å) and Ir−C≡ (2.042(9), 2.044(9) Å) bonds. These values may be compared with those for the complex [IrH(C≡CPh)$_2$(CO)(PPh$_3$)$_2$],[10] for which the two alkynyl ligands are related by crystallographic C_2 symmetry to provide Ir−C and −C≡C− bond lengths of 2.04(2) and 1.15(2) Å, respectively. Similar metallabutadiynyl bond localization has been observed for the mono(tricarbido) complexes [Re{C≡CC≡W(OCMe$_3$)$_3$}(NO)(PPh$_3$)(η-C$_5$Me$_5$)]$_2$[3] and [RuH(C≡CC≡W(CO)$_2${HB(pzMe$_2$)$_3$})(HpzMe$_2$)(CO)(PPh$_3$)$_2$];[5] however, the salt [Re{=C=C=C=Mn(CO)$_2$(η-C$_5$H$_5$)}(NO)(PPh$_3$)(η-C$_5$Me$_5$)]BF$_4$ shows a more regular "1,5-dimetallapentatetraene" pattern of bonding.[2]

Scheme 1. Synthesis of 1 (L = PPh$_3$, Tp = HB(pz)$_3$)



The formation of **1** rather than simple halide/acetylide metathesis to provide [{HB(pz)$_3$}(CO)$_2$W≡CC≡C−Ir(CO)(PPh$_3$)$_2$] (**2**) calls for comment (Scheme 1). We assume that **2** is most likely the initial product but that this reacts quickly with [W(≡CC≡CH)(CO)$_2${HB(pz)$_3$}] (generated in situ) via oxidative addition. This is itself noteworthy in that, as noted above, the synthesis of [Ir(C≡CPh)(CO)(PPh$_3$)$_2$] is performed in the presence of excess ethynylbenzene but does not proceed to [IrH(C≡CPh)$_2$(CO)(PPh$_3$)$_2$] under ambient conditions.[8,11] This complex was, however, obtained by Wilkinson from the reactions of excess ethynylbenzene with [IrH(CO)$_x$-

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[9] A suspension of [W(≡CC≡CSiMe$_3$)(CO)$_2${HB(pz)$_3$}][7] (200 mg, 0.36 mmol) and [IrCl(CO)(PPh$_3$)$_2$] (125 mg, 0.16 mmol) in CH$_2$Cl$_2$ (15 mL) was treated with [Bu$_4$N]F (0.71 mL, 1.0 M, Aldrich) and stirred for 2 h. The fine orange suspension was filtered, and the solid stirred in CH$_2$Cl$_2$ for 30 min. The resulting suspension was centrifuged, the supernatant discarded, and the solid dried in vacuo. Yield: 109 mg (40%). IR: in Nujol, ν 2127 (Ir−C≡C), 2017 (Ir−CO), 1949 (W−CO), 1860 (W−CO) cm^{-1}; in THF, 2139 (Ir−C≡C), 2019 (Ir−CO), 1948 (W−CO), 1873 (W−CO) cm^{-1}. NMR (d_6-DMSO, 25 °C): ^{1}H, δ 7.90−7.86 (m, 6 H, H^3 (pz)), 7.60−7.29 (m × 2, 36 H, H^5 (pz) + C$_6$H$_5$), 6.30−6.20 (m, 6 H, H^4 (pz)), −8.78 (t, $^2J_{PH}$ = 13.7 Hz, 1 H, Ir−H) ppm; ^{31}P{^{1}H}, −1.86 ppm. Anal. Found: C, 45.43; H, 2.96; N, 9.64. Calcd for C$_{65}$H$_{51}$B$_2$IrN$_{12}$O$_5$P$_2$W$_2$: C, 45.29; H, 2.98; N, 9.75. A sample for crystallographic analysis was recrystallized from a mixture of chloroform and ethanol as a bis(chloroform) solvate. Crystal data for **1**·2CHCl$_3$: C$_{65}$H$_{51}$B$_2$IrN$_{12}$O$_5$P$_2$W$_2$.(CHCl$_3$)$_2$, M_r = 1962.44, triclinic, $P\bar{1}$ (No. 2), a = 14.1710(2) Å, b = 14.4573(2) Å, c = 21.6538(3) Å, α = 97.021(1)°, β = 107.565(1)°, γ = 92.608(1)°, V = 4181.8(1) Å^3, Z = 2, ρ_{calcd} = 1.558 g cm^{-3}, μ(Mo Kα) = 4.611 mm^{-1}, T = 200 K, brown plate, 14 831 independent measured reflections (2θ ≤ 50°), R1 = 0.043, wR2 = 0.046 for 8559 independent observed absorption-corrected reflections (I > 3σ(I)), 874 parameters. CCDC 225193.

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$(PPh_3)_{4-x}$] (x = 1, 2) or [Ir(C≡CEt)(CO)$(PPh_3)_2$] in refluxing benzene.[13]

A further feature of note is the lowering of the tungsten−carbonyl associated infrared absorptions on replacing the $SiMe_3$ in the precursor (THF: ν(CO) 1991, 1906 cm^{-1}) with the iridium(III) center in **1** (THF: ν(CO) 1949, 1860 cm^{-1}).

Supporting Information Available: Full details of the crystal structure determination of **1**·$2CHCl_3$, 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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