Polycarbon Bridges

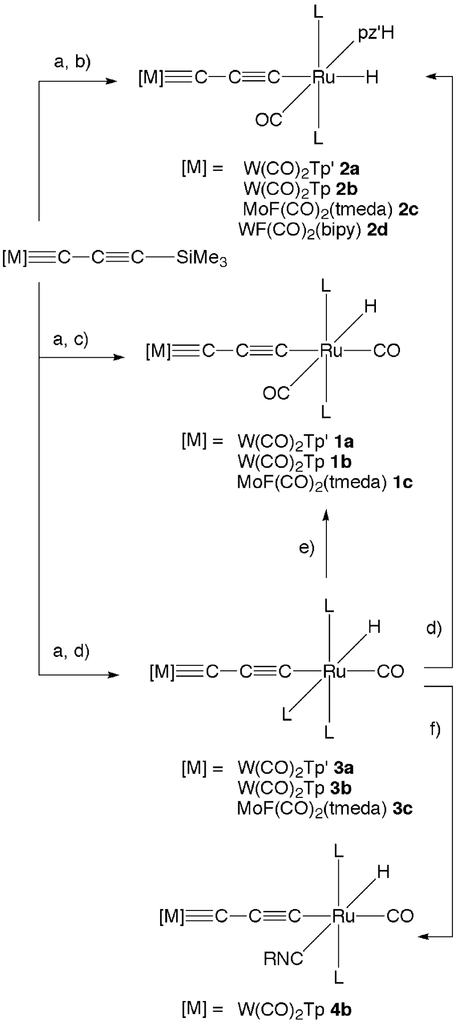
Heterobimetallic C_3 Complexes through Silylpropargylidyne Desilylation

Rian D. Dewhurst, Anthony F. Hill, and Matthew K. Smith*

Dedicated to Professor Michael I. Bruce on the occasion of his 65th birthday

Although the chemistry of bimetallic compounds bridged by linear polycarbon ligands, $L_nM(C_x)ML_n$, has grown at an enormous pace,[1] there remains a hiatus for odd-numbered examples ($x = 3, 5, 7\ldots$). It would be premature to attribute this to any inherent instability, though this may well eventually prove to be a contributing factor.[2] Rather, at present, it is a reflection of the majority of synthetic strategies that commence with free polyynes $R(C_2)_{x/2}R$ ($R = H$, $SiMe_3$) or metal poly(ynyls) $L_nM(C_2)_{x/2}R$, each of which by necessity lead to even-numbered carbon chains. Bimetallic compounds spanned by linear C_3 ligands are limited to: 1) $[(\eta\text{-}C_5Me_5)(NO)(PPh_3)Re\text{-}C{\equiv}C\text{-}C{\equiv}ML_n]$ ($ML_n = \{Fe(CO)_4\}^+$; $\{Mn(CO)_2(\eta\text{-}C_5H_mCl_{5-m})\}^+$ $m = 0, 1, 5$; $W(OtBu_3)_3$), which arise from Fischer-type carbyne syntheses commencing with $[(\eta\text{-}C_5Me_5)(NO)(PPh_3)Re\text{-}C{\equiv}C\text{-}Li]$ and the appropriate metal carbonyl,[3a,b] or alkyne metathesis of the diynyl complexes $[(\eta\text{-}C_5Me_5)(NO)(PPh_3)Re\text{-}C{\equiv}C\text{-}C{\equiv}CR]$ ($R = H$, Me) with $[W_2(OtBu)_6]$,[3c] as described by Gladysz and co-workers; and 2) $[Tp'(CO)_2M{\equiv}C\text{-}C{\equiv}C\text{-}M'({=}O)_2Tp']$ (M, M′ = Mo, W; Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate) obtained by Templeton and Woodworth through deprotonation of $[Tp'(CO)_2M{\equiv}C\text{-}CH_2C{\equiv}M'(CO)_2Tp']$ under aerobic conditions.[4] Whilst these were each ground-breaking in establishing the viability of this class of compound, the routes at present lack generality and the metal centers involved are inert to substitution. Herein we report two synthetic strategies for the construction of a range of $L_nMC_3ML_n$ complexes which offer scope for extension to many metals.

We previously described convenient synthetic routes to a range of propargylidyne complexes of the Group 6 metals, $L_nM{\equiv}C\text{-}C{\equiv}CCMe_3$ (M = Mo, W).[5] Fischer and co-workers recently extended this protocol to include silylated examples $L_nM{\equiv}C\text{-}C{\equiv}CSiMe_3$ and suggested that they might be prone to desilylation.[6] As fluorodesilylation of alkynyl silanes is a widely employed synthetic protocol, we envisaged that silylpropargylidynes might serve as suitable reagents for constructing $L_nM{\equiv}C\text{-}C{\equiv}C\text{-}ML_n$ linkages. Towards this end, the reaction of $[Tp'(CO)_2W{\equiv}C\text{-}C{\equiv}CSiMe_3]$[6a] with $[Bu_4N]F$ was investigated in the presence of $[Ru(CO)_2(PPh_3)_3]$, a complex that is known to oxidatively add terminal alkynes.[7] From this reaction, the bimetallic complex $[Tp'(CO)_2W{\equiv}C\text{-}C{\equiv}C\text{-}RuH(CO)_2(PPh_3)_2]$ (**1a**) was readily isolated in modest yield, implicating the intermediacy of the parent propargylidyne complex $[Tp'(CO)_2W{\equiv}C\text{-}C{\equiv}CH]$ (Scheme 1) consistent with the suggestion of Fischer and co-workers.[6a]



Scheme 1. L = PPh₃, R = 2,4,6 $Me_3C_6H_2$, [M] = $W(CO)_2Tp$, $W(CO)_2Tp'$, $MoF(CO)_2(tmeda)$, $WF(CO)_2(bipy)$ (not all combinations). a) $[Bu_4N]F$; b) $[RuHCl(CO)(Hpz')L_2]$; c) $[Ru(CO)_2L_3]$; d) $[RuH(NCMe)_2(CO)L_2]BF_4$ or $[RuHCl(CO)L_3]$; e) CO; f) Hpz′; g) CNR. tmeda = tetramethylethylenediamine, bipy = bipyridyl.

As an alternative to the oxidative addition approach, the possibility of deploying nucleophilic anions $[L_nM{\equiv}C\text{-}C{\equiv}C][Bu_4N]$, generated in situ, for halide metathesis reactions was investigated, although no attempt was made to isolate these intermediate species. Treatment of a range of silylpropargylidynes with $[Bu_4N]F$ in the presence of the hydrido complex $[RuHCl(CO)(Hpz')(PPh_3)_2]$ (Hpz′ = 3,5-dimethylpyrazole)[8] provided the bimetallic complexes $[L_nM{\equiv}C\text{-}C{\equiv}C\text{-}RuH(CO)(Hpz')(PPh_3)_2]$ ($L_nM = W(CO)_2Tp'$ (**2a**), $W(CO)_2Tp$ (**2b**, Tp = hydrotris(pyrazolyl)borate), $MoF(CO)_2(tmeda)$

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(**2c**), $WF(bipy)(CO)_2$ (**2d**)). Notably, when trifluoroacetato complexes $[Mo(\equiv C{-}C\equiv CSiMe_3)(O_2CCF_3)(CO)_2(tmeda)]$ and $[W(\equiv C{-}C\equiv CSiMe_3)(O_2CCF_3)(CO)_2(bipy)]$ were employed, CF_3CO_2/F metathesis also occurred at the Group 6 metal center. The complex $[RuHCl(CO)(PPh_3)_3]$[9] has been shown to react with $LiC\equiv C\textit{t}Bu$ to provide $[RuH(C\equiv C\textit{t}Bu)(CO)(PPh_3)_3]$,[10] and the related set of C_3-bridged complexes $[L_nM\equiv C{-}C\equiv CRuH(CO)(PPh_3)_3]$ ($L_nM = W(CO)_2Tp'$ (**3a**), $W(CO)_2Tp$ (**3b**), $MoF(CO)_2(tmeda)$ (**3c**)) were readily prepared by reaction of the appropriate silylpropargylidyne with $[Bu_4N]F$ and $[RuHCl(CO)(PPh_3)_3]$. Unexpectedly, we first observed these same products spectroscopically from similar treatment of the $[RuH(NCMe)_2(CO)(PPh_3)_2]BF_4$ salt, presumably via phosphane redistribution. The lability of one phosphane ligand could be demonstrated by reactions with CO, Hpz', or 2,4,6-Me_3-CNC_6H_2 to provide $[L_nM\equiv C{-}C\equiv C\text{-}RuH(CO)(L)(PPh_3)_2]$ (L = CO (**1**), Hpz' (**2**), 2,4,6-Me_3-CNC_6H_2 (**4**)). The complex $[RuHCl(CO)(PPh_3)_3]$ readily hydrometallates alkynes,[11] diynes,[12] and phosphaalkynes,[13] and so it is noteworthy that halide metathesis occurs instead under the present reactions.

The hydride ligand in these complexes serves as a useful "reporter" ligand for NMR spectroscopic analysis, reinforcing the assignments for the MC_3Ru spines. Thus, $^1H,^{13}C$-HMBC NMR spectra acquired for the complexes indicate coupling between the hydride nucleus and the three carbon nuclei. This is illustrated for the complex **1b** (Figure 1) for which correlations are observed for a) $W\equiv C{-}C\equiv C$-Ru, b) and c) $Ru(CO)_2$, d) $W\equiv C{-}C\equiv C$-Ru, e) $C^1(PC_6H_5)$, f) $C^{2,6}(PC_6H_5)$, and g) $W\equiv C{-}C\equiv C$-Ru. The chemical shifts of the three bridging carbon nuclei, namely $\delta = 260.6$ ($W\equiv C{-}C\equiv C$-Ru), 138.6 ($W\equiv C{-}C\equiv C$-Ru) and 118.7 ppm ($W\equiv C{-}C\equiv C$-Ru) are consistent with a somewhat localized $W\equiv C{-}C\equiv C$-Ru bonding description.

The complex **2a** was the subject of a crystallographic study,[14] the results of which are summarized in Figure 2. The molecular structure confirms the pseudooctahedral geometries at both the tungsten and ruthenium centers and establishes the *trans*-$HRuC\equiv C$ stereochemistry, the hydride ligand having been located and satisfactorily refined. Interest focuses on the essentially linear W(sp-C)$_3$Ru spine, the geometric parameters of which conform to a $W\equiv C{-}C\equiv C$-Ru valence bond description akin to that suggested for $\{(\eta\text{-}C_5Me_5)(NO)(PPh_3)Re\text{-}C\equiv C{-}C\equiv W(O\textit{t}Bu)_3\}_2$[3b] rather than the more cumulenic salt $\{(\eta\text{-}C_5Me_5)(NO)(PPh_3)Re{=}C{=}C{=}C{=}Mn(CO)_2(\eta\text{-}C_5H_5)]BF_4$.[3c] Thus, the $W\equiv C$ separation of 1.848(5) Å is typical of those observed for tungsten alkylidynes,[15] and the Ru1-C3 bond length of 2.096(5) Å falls within the range noted for ruthenium alkynyls.[16] The C2-C3 [1.230(7)] and C2-C1 [1.373(7) Å] lengths correspond to essentially localized triple and single bonds between two coordinated carbon centers.

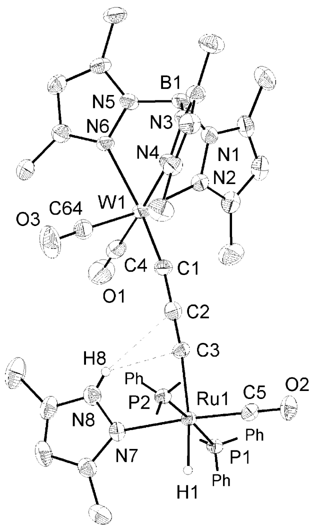

Figure 2. Molecular geometry of **2a** (phenyl groups omitted). Selected distances [Å] and angles [°]: Ru1-C3 2.096(5), C3-C2 1.230(7), C2-C1 1.373(7), W1-C1 1.848(5), W1-N4 2.230(4), W1-N2 2.206(4), W1-N6 2.300(4), Ru1-H 1.56(6), H8-C3 2.28(5), H8-C2 2.59(5), W1-Ru1 6.515(2), Ru1-C3-C2 175.0(4), C1-C2-C3 178.9(5), W1-C1-C2 171.2(4).

In summary, we have shown that silylpropargylidynes can serve as useful precursors for the construction of linear C_3-bridged bimetallic compounds through two complementary routes: 1) in situ generation of terminal propargylidyne complexes for subsequent oxidative addition ($\equiv$C-H activation) or 2) in situ generation of propargylidynyl nucleophiles for metathesis with metal halides. Although a dozen new examples of linear C_3-bridged bimetallic complexes have resulted, they all contain $M\equiv C{-}C\equiv C$-Ru (M = Mo, W) spines. Accordingly, we are currently exploring the generality of this protocol with respect to extension to other metal centers.

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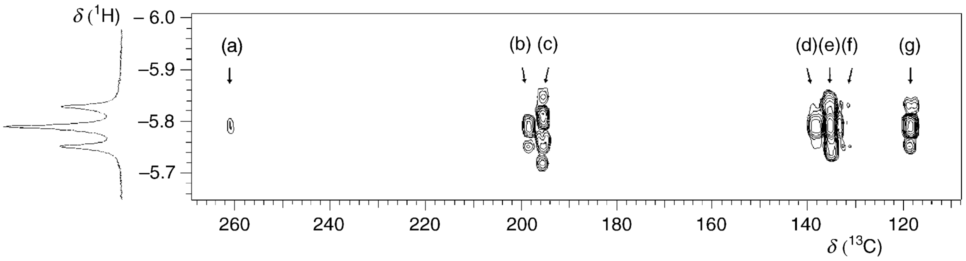

Figure 1. $^{13}C,^{1}H$-HMBC NMR spectrum ($\delta < 0$) for $[Tp(CO)_2W\equiv C{-}C\equiv C\text{-}RuH(CO)_2(PPh_3)_2]$ (**1b**) optimized for 2 Hz $^1H-^{13}C$ coupling.

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[14] Crystal data for **2a**: $C_{64}H_{65}BCl_4N_8O_3P_2RuW$, $M_w = 1493.7$, triclinic, $P\bar{1}$ (no. 2), $a = 9.788(1)$, $b = 15.125(1)$, $c = 22.850(1)$ Å, $\alpha = 72.050(1)$, $\beta = 88.365(1)$, $\gamma = 88.699(1)°$, $V = 3216.5(4)$ Å^3, $Z = 2$, $T = 200(2)$ K, $\rho_{\text{cald}} = 1.542\ \text{g cm}^{-3}$, $\text{Mo}_{K\alpha}$ radiation, $\mu = 2.289\ \text{mm}^{-1}$, yellow rod $0.36 \times 0.15 \times 0.05\ \text{mm}^3$; 14738 independent measured reflections, F^2 refinement, $R_1 = 0.046$, $wR_2 = 0.107$, 11888 independent observed absorption-corrected reflections ($I > 2\sigma(I)$), $2\theta = 55.1°$], 778 parameters. CCDC-217762 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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