Carbynes Generated from Metal Carbonyl and Isocyanide Complexes: Intermediates in the Reductive Coupling of CO and CNR Ligands

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Previously we reported the reductive coupling of alkyl isocyanide ligands in seven-coordinate $[M(CNR)_6X]^+$ (M = Mo or W; X = halide or cyanide)[1] and $[Mo(CNR)_5(bpy)]^{2+}$ [2] complexes (eq 1 and 2) and of carbonyl ligands in heptacoordinate $[M(CO)_2(dmpe)_2Cl]$ [M = Nb (**1**) or Ta (**2**); dmpe = 1,2-bis(dimethylphosphino)ethane][3] complexes (eq 3) to form coordinated alkynes.

$$[M(CNR)_6X]^+ + Zn(s) \xrightarrow[H^+]{THF} [M(RHNCCNHR)(CNR)_4X]^+ \quad (1)$$

$$[Mo(CNR)_5(bpy)]^{2+} + Zn(s) \xrightarrow[H^+]{THF} [Mo(RHNCCNHR)(CNR)_3(bpy)]^{2+} \quad (2)$$

$$\underset{M = Nb,\ \mathbf{1};\ Ta,\ \mathbf{2}}{[M(CO)_2(dmpe)_2Cl]} \xrightarrow[THF]{40\%\ Na/Hg} \xrightarrow{2\ Me_3SiCl} \underset{M = Nb,\ \mathbf{3};\ Ta,\ \mathbf{4}}{[M(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]} \quad (3)$$

Here we describe the isolation and structural characterization of a key intermediate in the reductive coupling of CO, namely, the trialkylsiloxycarbynes $[M(CO)\{COSi(i\text{-}Pr)_3\}(dmpe)_2]$ [M = Nb (**5**) or Ta (**6**)]. We further observe conversion of these unprecedented molecules via carbonyl–carbyne coupling to give bound acetylene diethers (cf. eq 3). Also reported is that alkylaminocarbynes $[Re(CNHR)(CNR)_2(PMePh_2)_2Cl]^+$ [R = *t*-Bu (**7**) or Me (**8**)] are generated from $[Re(CNR)_3(PMePh_2)_2Cl_2]^+$ cations[4] under conditions that gave reductive coupling in eq 1 and 2.[1,2] These results strongly suggest that eq 1–3 all proceed by a common mechanistic pathway involving carbyne intermediates.

When $[Ta(CO)_2(dmpe)_2Cl]$ (**2**) dissolved in THF was allowed to react in a nitrogen-filled drybox with excess 40% sodium amalgam for 4.5 h, the sodium salt of *cis*-$[Ta(CO)_2(dmpe)_2]^-$ is formed.[3b] Addition of 1 equiv of $(i\text{-}Pr)_3SiCl$ to this solution resulted in a color change from red-brown to plum-red. Removal of solvent in vacuo and reprecipitation from Me_4Si (TMS) gave $[Ta(CO)\{COSi(i\text{-}Pr)_3\}(dmpe)_2]$ (**6**, 90% crude yield, >90% pure by ^{31}P and ^1H NMR).[5] The procedure was also applied to synthesize the niobium analogue **5** in 94% crude yield by starting with **1**.[6] In analogous chemistry, the *tert*-butylaminocarbyne rhenium complex **7** was generated by refluxing a mixture containing $[Re(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2Cl_2]Cl$, excess Zn, catalytic $ZnCl_2$, excess $KSbF_6$, and traces of H_2O, in THF for 6 h under N_2. The solution was allowed to cool to room temperature, filtered, and evaporated to dryness under N_2. Recrystallization of the residue at −30 °C from dichloromethane/pentane yielded 71% of crystalline yellow $[Re(CNH\text{-}t\text{-}Bu)(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2Cl](SbF_6)$.[7]

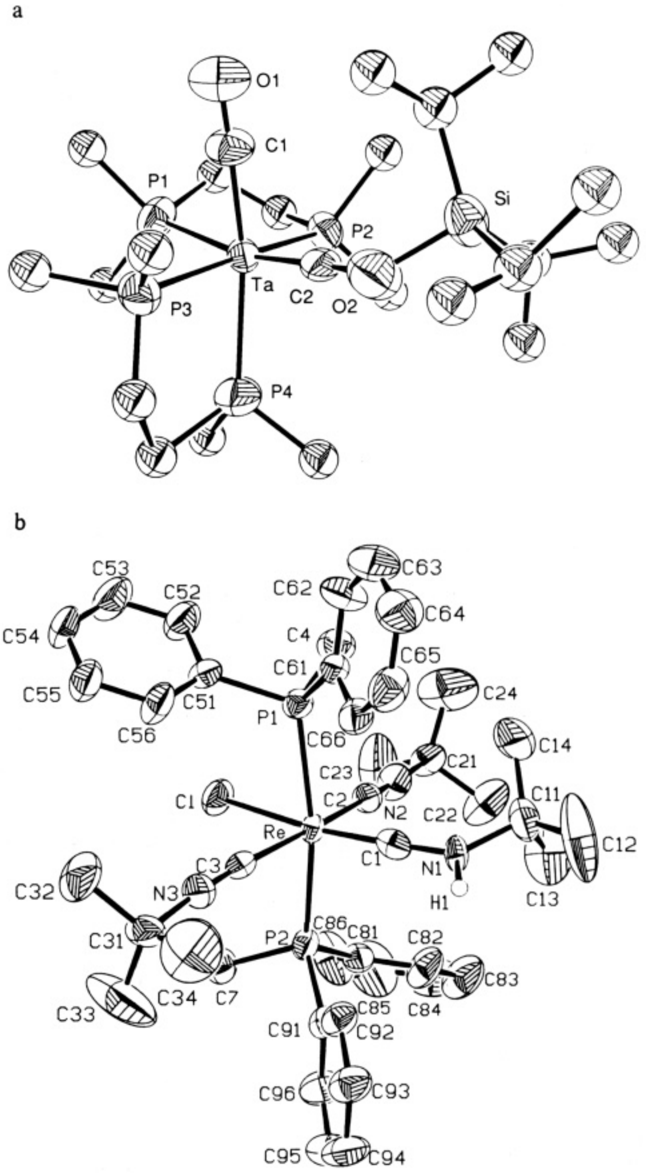

Figure 1. Structures of (a) $[Ta(CO)\{COSi(i\text{-}Pr)_3\}(dmpe)_2]$ (**6**) and (b) $[Re(CNH\text{-}t\text{-}Bu)(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2Cl]^+$ (**7**). For clarity, methyl and methylene carbon atoms of **6** are depicted as spheres with $B = 5.0$ Å^2, and only one orientation of a disordered isopropyl fragment is drawn. All other atoms show anisotropic thermal ellipsoids at 40% probability. Selected bond distances (Å) and angles (deg) are as follows: For **6** [and **5**, in square brackets], Ta–C1, 2.00 (2) [2.01 (1)]; Ta–C2, 1.85 (1) [1.88 (1)]; Ta–P1, 2.635 (4) [2.668 (3)]; Ta–P2, 2.506 (4) [2.531 (3)]; Ta–P3, 2.490 (4) [2.505 (3)]; Ta–P4, 2.538 (4) [2.547 (3)]; C1–O1, 1.20 (2) [1.17 (1)]; C2–O2, 1.34 (2) [1.34 (1)]; O2–Si, 1.69 (1) [1.680 (8)]; Ta–C2–O2, 173 (1) [172.7 (8)]; C2–O2–Si, 128 (1) [126.9 (7)]. For **7**, Re–C1, 1.82 (1); Re–C2, 2.05 (1); Re–C3, 2.07 (1); Re–Cl, 2.497 (3); Re–P1, 2.453 (3); Re–P2, 2.428 (3); C1–N1, 1.30 (1); N1–C11, 1.48 (1); Re–C1–N1, 175.7 (9); C1–N1–C11, 127.6 (9).

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[5] Anal. Calcd for $C_{23}H_{53}O_2P_4SiTa$ (**6**, recrystallized from Me_4Si at −30 °C): C, 39.77; H, 7.69; P, 17.84; Si, 4.04. Found: C, 38.92; H, 7.58; P, 17.60; Si 4.26. Spectroscopic data: FTIR (KBr) 1775, 1742, 1307 cm^{-1}; ^{31}P NMR (161.9 MHz, C_6D_6, referenced to external 85% H_3PO_4) δ 25.4, 24.7, 11.7, −0.6 ppm; ^1H NMR (300 MHz, C_6D_6) δ 0.64 (d, $J_{P-H} = 3.2$ Hz, PCH_3), 0.96 (d, $J_{P-H} = 3.5$ Hz, PCH_3), 1.54–1.20 (m, 41 protons), 1.80 (d, $J_{P-H} = 6.8$ Hz, PCH_3), 1.84 (d, $J_{P-H} = 6.9$ Hz, PCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 253.15 (s, $\equiv$COSi), 243.37 (s, CO).

[6] Spectroscopic data for **5**, recrystallized from Me_4Si at −30 °C: FTIR (KBr) 1780, 1740, 1294 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.62 (d, $J_{P-H} = 2.46$ Hz, PCH_3), 0.90 (d, $J_{P-H} = 2.76$ Hz, PCH_3), 1.10–1.55 (m, 41 H), 1.86 (d, $J_{P-H} = 5.89$ Hz, PCH_3), 1.73 (d, $J_{P-H} = 5.82$ Hz, PCH_3).

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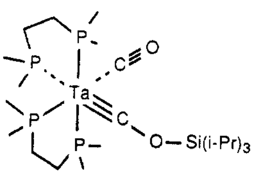
Figure 1 displays the structures of **6**[8] and **7**,[9] including some metrical data. The Ta–C bond length of 1.85 (1) Å in **6** is identical with the value reported for the alkylidyne complex $[Ta(CPh)(\eta\text{-}C_5H_5)(PMe_3)Cl]$[10] and appreciably shorter than distances found for compounds having tantalum–carbon single (2.25–2.32 Å) and double (2.01–2.03 Å) bonds.[11] The C–OSiR$_3$ distances of 1.34 (1) Å in **5** and **6** are significantly longer than the respective values of 1.17 (1) and 1.20 (1) Å for the C–O bond lengths in the terminal carbonyl ligands, further substantiating the assignment of these molecules as trialkylsiloxycarbynes ($M{\equiv}C\text{-}OSiR_3$). Similar arguments may be used to assign cation **7** as an alkylaminocarbyne, the $Re{\equiv}C$ bond length of 1.82 (1) Å being close to the 1.80 (3) Å value previously reported for *trans*-$[Re(CNHMe)(dppe)_2Cl](BF_4)$.[12] The strong trans influence of the $M{\equiv}C$ bond in these complexes is nicely illustrated by the 0.13 Å average increase in the trans compared to the cis M–P distances in **5** and **6**. Four multiplets in the ^{31}P NMR spectrum of **6**[5] dissolved in benzene-d_6 can be fit to an ABMX splitting pattern, indicating that the solid-state structure is retained in solution.



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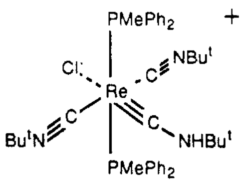

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Coupling of the carbyne and carbonyl ligands in **5** and **6** was accomplished by allowing them to react in THF or glyme with 1 equiv of either Me_3SiCl or $(i\text{-}Pr)_3Si(OTf)$, eq 4. Coupling of

$$[M(CO)\{COSi(i\text{-}Pr)_3\}(dmpe)_2] + R_3SiY \rightarrow [M\{R_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Y] \quad (4)$$

$$M = Nb,Ta;\ R = Me,\ Y = Cl;\ R = i\text{-}Pr,\ Y = OTf$$

carbonyl with carbyne ligands has been observed for a number of tungsten complexes.[13] Attempts to achieve isocyanide–carbyne coupling by addition of excess HX (X = Cl, Br, or I) to solutions of **7** resulted in no reaction for X = Cl and halide exchange for X = Br or I. Nevertheless, isolation of **7** and **8** under reductive coupling conditions used in analogous Mo(II) and W(II) chemistry (eq 1 and 2)[1,2] and the identification of **5** and **6** as intermediates in eq 3 strongly suggest that alkylaminocarbynes are involved in the reductive coupling of isocyanides.

In conclusion, we find that the reductive coupling of carbon monoxide in $[M(CO)_2(dmpe)_2Cl]$, M = Nb, Ta, to form coordinated bis(trialkylsiloxy)ethyne proceeds through siloxycarbyne intermediates. Although conversion of a thiocarbonyl ligand into a mercaptocarbyne by electrophilic attack at sulfur is known,[14] the present examples are the first where a carbonyl ligand has been so converted into an oxycarbyne bound to a single metal center. This discovery might provide some insight into the chemistry of other CO conversions, such as the Fischer–Tropsch reaction.

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Registry No. 1, 66507-17-3; **2**, 61916-36-7; **5**, 113380-13-5; **6**, 113380-14-6; **7**, 113380-16-8; *cis*-$[Ta(CO)_2(dmpe)_2]Na$, 61916-37-8; *cis*-$[Nb(CO)_2(dmpe)_2]Na$, 113380-12-4; $[Re(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2Cl_2]Cl$, 113380-17-9; $[Nb\{Me_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Cl]$, 113380-18-0; $[Ta\{Me_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2Cl]$, 113380-19-1; $[Nb\{(i\text{-}Pr)_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2OTF]$, 113380-20-4; $[Ta\{(i\text{-}Pr)_3SiOCCOSi(i\text{-}Pr)_3\}(dmpe)_2OTF]$, 113380-21-5; $(i\text{-}Pr)_3SiCl$, 13154-24-0; Me_3SiCl, 75-77-4; $(i\text{-}Pr)_3Si(OTF)$, 80522-42-5.

Supplementary Material Available: Atomic positional and thermal parameters for **5**, **6**, and **7** (6 pages). Ordering information is given on any current masthead page.

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(7) Anal. Calcd for $C_{41}H_{54}N_3P_2ClReSbF_6$: C, 44.44; H, 4.91; N, 3.79. Found: C, 43.27, 45.36; H, 4.98, 4.93; N, 3.88, 3.69. Spectroscopic data: FTIR (KBr) 2147 (s), 1588 (s) cm^{-1}; ^1H NMR (90 MHz, CD_2Cl_2) δ 0.65 (s, 9 H, $CNH(CH_3)_3$, 1.14 (s, 18 H, $CN(CH_3)_3$), 2.25 (virtual t, 6 H, PCH_3), 4.52 (br, 1 H, CN*H*-*t*-Bu), 7.40–7.46 (m, 20 H, $P(C_6H_5)$); $^{13}C\{^1H\}$ NMR (75.43 MHz, CD_2Cl_2) δ 16.58 (virtual t, PCH_3), 29.57 (s, $CNHC(CH_3)_3$), 29.94 (s, $CNC(CH_3)_3$), 58.32 (s, CN*C*Me$_3$ and CNH*C*Me$_3$), 128.74 (virtual t, P-*m*-Ph), 130.34 (s, P-*p*-Ph), 132.58 (virtual t, P-*o*-Ph), 136.03 (virtual t, P-ipso-Ph), 143.15 (t, $^2J_{PC}$ = 9.1 Hz, *C*NCMe$_3$), 227.54 (t, $^2J_{PC}$ = 11.3 Hz, *C*NH-*t*-Bu); $^{31}P\{^1H\}$ NMR (36.6 Hz, CD_2Cl_2) δ −11.0.

(8) Crystal data for **6**: $C_{23}H_{53}O_2P_4SiTa$, M_r = 694.6, monoclinic, space group $P2_1/c$, a = 9.836 (2) Å, b = 30.154 (4) Å, c = 12.248 (2) Å, β = 112.53 (2)°, V = 3355.4 Å^3, Z = 4, ρ_{calcd} = 1.375 g cm^{-3}; R_F = 0.048. The Nb analogue is isomorphous [a = 9.821 (4) Å, b = 30.273 (7) Å, c = 12.236 (3) Å, β = 112.47 (2)°, V = 3361.5 Å^3; R_F = 0.046]. Some disorder occurs for the isopropyl and dmpe ethylene groups in both structures and refinement is continuing. Full details will be reported elsewhere.

(9) Crystal data for **7**: $C_{41}H_{54}N_3P_2ClSbF_6Re$, M_r = 1108.2, monoclinic, space group $P2_1/c$, a = 15.378 (3) Å, b = 18.731 (3) Å, c = 16.225 (3) Å, β = 95.94 (1)°, V = 4648.4 Å^3, Z = 4 ρ_{calcd} = 1.584 g cm^{-3}, ρ_{obsd} = 1.58 (1) g cm^{-3}; R_F = 0.042. Details will be described in a separate report.

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Intramolecular Excited-State Electron Transfer in a Covalently Linked Porphyrin-Viologen Molecule: Direct Observation of the Charge-Separated Intermediate by Resonance Raman Spectroscopy

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We wish to report the observation of intramolecular excited-state electron transfer in porphyrin–viologen **1** by resonance Raman (RR) spectroscopy. The literature contains numerous examples of photochemical studies of porphyrins covalently linked to various electron acceptor units.[2-4] Other workers have investigated long-range excited-state electron transfer in rigid model systems.[5] In many instances, electron-transfer quenching of the porphyrin excited state has been inferred from fluorescence quenching experiments or lifetime measurements.[2] Both

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