A terminal molybdenum carbide prepared by methylidyne deprotonation

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The carbide anion $[\mathrm{CMo\{N(R)Ar\}_3}]^-$ [R = $\mathrm{C(CD_3)_2CH_3}$, Ar = $\mathrm{C_6H_3Me_2}$-3,5], is obtained by deprotonation of the corresponding methylidyne compound, $[\mathrm{HCMo\{N(R)Ar\}_3}]$, and is characterized by X-ray diffraction as its $\{\mathrm{K(benzo\text{-}15\text{-}crown\text{-}5)_2}\}^+$ salt, thereby providing precedent for the carbon atom as a terminal substituent in transition-metal chemistry.

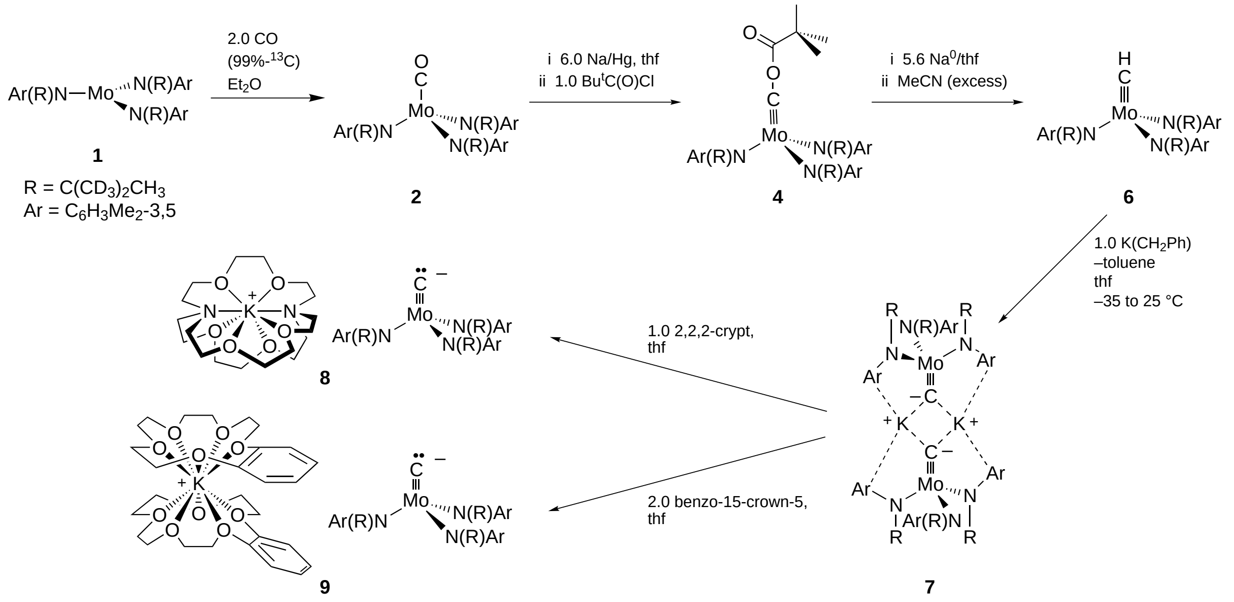
Recent work has shown that the molybdenum–nitrogen multiple bond in the nitride species $[\mathrm{NMo\{N(R)Ar\}_3}]$ [R = $\mathrm{C(CD_3)_2CH_3}$, Ar = $\mathrm{C_6H_3Me_2}$-3,5] is exceedingly strong, and that this complex is quite robust.[1,2] Recognizing that the anionic carbide $[\mathrm{CMo\{N(R)Ar\}_3}]^-$ would be isoelectronic with $[\mathrm{NMo\{N(R)Ar\}_3}]$, we set out to synthesize it. As described herein, a successful synthesis was accomplished *via* deprotonation of the d^0 methylidyne complex $[\mathrm{HCMo\{N(R)Ar\}_3}]$. Previously reported molecular carbide complexes feature carbon atoms with at least two nearest neighbors.[3–10]

Three-coordinate $[\mathrm{Mo\{N(R)Ar\}_3}]$ **1** was treated with 99% ^{13}C carbon monoxide to give the paramagnetic (μ_{eff} = 1.73 μ_{B}) carbonyl complex $[\mathrm{(O^{13}C)Mo\{N(R)Ar\}_3}]$ **2** (ν_{CO} 1797 cm^{-1}) as a brown solid in 88% yield.‡§ One-electron reduction of **2** was effected with sodium amalgam in tetrahydrofuran (thf) giving $[\mathrm{(NaO^{13}C)Mo\{N(R)Ar\}_3}]_2$ **3** [$\delta(^{13}\mathrm{C})$ 243.0] in essentially quantitative yield. **3** was obtained either as a solvent-free dimer or as an ether or thf solvate. *In situ* generated **3** was found to be sufficiently pure for synthetic purposes. Reaction of **3** with pivaloyl chloride[11] provided the 'carbido pivalate' complex $[\mathrm{Bu^tC(O)O(^{13}C)Mo\{N(R)Ar\}_3}]$ **4** [$\delta(^{13}\mathrm{C})$ 217.2] in 82% yield as a beige crystalline solid.¶ Removal of the pivalate moiety in **4** was effected by treatment with sodium in thf giving, according to ^{13}C NMR analysis, a mixture of 'sodium carbide' $[\mathrm{Na(^{13}C)Mo\{N(R)Ar\}_3}]_2$ **5** [$\delta(^{13}\mathrm{C})$ 474.2], methylidyne $[\mathrm{H(^{13}C)Mo\{N(R)Ar\}_3}]$ **6** [$\delta(^{13}\mathrm{C})$ 287.5, $^1J_{\mathrm{CH}}$ 157 Hz] and **3**. Treatment of the mixture with an excess of acetonitrile converted **5** to **6**, solubilized **3** and precipitated **6** in essentially pure form. Methylidyne **6**, an off-white solid, was isolated by this procedure in 53% yield from **2**.‖ Several other routes to the terminal methylidyne functionality have been documented.[12–17]

Deprotonation of **6** was effected by benzylpotassium in thf,[18] giving the potassium–molybdenum carbido complex $[\mathrm{K(^{13}C)Mo\{N(R)Ar\}_3}]_2$ **7** [$\delta(^{13}\mathrm{C})$ 494.5][19,20] in 69% yield after recrystallization from pentane–thf.** In thf solution **7** presumably exists as a thf solvate, but the indicated thf-free, benzene-soluble dimer stabilized by intramolecular K$^+$–arene interactions[21] is readily obtained. Dimer **7** has been shown by X-ray crystallography to possess a central $\mathrm{K_2(carbide)_2}$ square array situated about a crystallograpic inversion center.[22,23]

Treatment in thf of the potassium–molybdenum carbide **7** with 2,2,2-crypt[24] led to formation of the thf-soluble, benzene-insoluble salt $[\mathrm{K(2,2,2\text{-}crypt)}][\mathrm{^{13}CMo\{N(R)Ar\}_3}]$ **8** [$\delta(^{13}\mathrm{C})$ 482.8].†† The ^{1}H NMR spectrum of **8** in [^{2}H$_8$]thf showed the expected four sharp resonances for the threefold-symmetric anion, along with the three signals characteristic of the $[\mathrm{K(2,2,2\text{-}crypt)}]^+$ cation. The curious fact that the ^{13}C NMR signal for the carbido carbon in **8** is broad ([^{2}H$_8$]thf, $\Delta\nu_{1/2}$ 1400 Hz) contrasts with the situation for **7**, which (in $\mathrm{C_6D_6}$) exhibits a sharp signal.

A salt of the $[\mathrm{CMo\{N(R)Ar\}_3}]^-$ anion amenable to X-ray crystallography, **9**, was obtained upon treatment of **7** with 2 equiv. (per K) of benzo-15-crown-5.[25] Crystals of salt **9**, which exhibited solubility characteristics similar to **8**, were obtained from thf–pentane.‡‡ The X-ray diffraction study of **9** revealed discrete and separate $[\mathrm{CMo\{N(R)Ar\}_3}]^-$ anions and $[\mathrm{K(benzo\text{-}15\text{-}crown\text{-}5)_2}]^+$ cations (Fig. 1).§§ The molybdenum–carbon distance in **9** was found to be 1.713(9) Å, at the low end of the known range for Mo–C multiple bonds.[26] The three N(R)Ar



Scheme 1

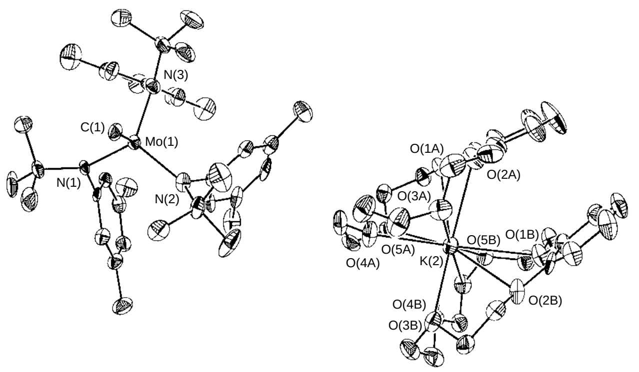


Fig. 1 Structural representation of [K(benzo-15-crown-5)$_2$][CMo{N-(R)Ar}$_3$] **9** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 1.713(9), Mo(1)–N(1) 2.008(6), Mo(1)–N(2) 2.010(7), Mo(1)–N(3) 2.013(6); C(1)–Mo(1)–N(1) 102.7(3), C(1)–Mo(1)–N(2) 103.9(3), N(1)–Mo(1)–N(2) 114.7(3), C(1)–Mo(1)–N(3) 103.8(3), N(1)–Mo(1)–N(3) 116.9(3), N(2)–Mo(1)–N(3) 112.6(3).

ligands in [CMo{N(R)Ar}$_3$]$^-$ adopt a propeller motif with the aryl rings π stacked[27] on one side of the molecule and the *tert*-butyl groups on the other side forming a protective 'pocket' about the Mo–C multiple bond. The gross structural and conformational features of [CMo{N(R)Ar}$_3$]$^-$ were anticipated based on structures of the related nitrido and phosphido derivatives [NMo{N(Bu^t)Ph}$_3$][1] and [PMo{N(R)Ar}$_3$].[28]

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Footnotes and References

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‡ All manipulations were carried out under an atmosphere of dry nitrogen using solvents purified by standard methods.

§ *Other data* for **2**: ^{2}H NMR (46 MHz, pentane, 25 °C); δ 8.0 [s, $\Delta\nu_{1/2}$ 14 Hz, C(CD$_3$)$_2$]; μ_{eff} (300 MHz, 25 °C, C$_6$D$_6$) = 2.2 μ_{B}. FTIR (heptane, KBr); ν(^{13}CO) 1797 cm^{-1}. Anal. Calc. for $C_{37}H_{36}D_{18}MoN_3O$: C, 66.24; H, 8.11; N, 6.26. Found: C, 65.85; H, 8.44; N, 6.19%.

¶ The reaction to produce **4** was carried out using 6.5 mmol of **2**. *Other data* for **4**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C); δ 6.67 (s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 6.09 (s, 6 H, C$_6$*H*$_3$Me$_2$ *o*-H), 2.10 (s, 18 H, C$_6$H$_3$*Me*$_2$), 1.50 [s, 9 H, C(CD$_3$)$_2$C*H*$_3$], 1.22 [s, 9 H, C(C*H*$_3$)$_3$]. Anal. Calc. for $C_{42}H_{45}D_{18}MoN_3O_2$: C, 66.73; H, 8.40; N, 5.56. Found: C, 66.64; H, 8.24; N, 5.79%.

‖ The reaction to produce **6** was carried out using 2.66 mmol of **4**. *Other data* for **6**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C); δ 6.64 (s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 6.00 (s, 6 H, C$_6$*H*$_3$Me$_2$, *o*-H), 5.66 [d, 1 H, Mo(CH), $^1J_{\mathrm{CH}}$ 157 Hz], 2.07 (s, 18 H, C$_6$H$_3$*Me*$_2$), 1.49 [s, 9 H, C(CD$_3$)$_2$C*H*$_3$]. Anal. Calc. for $C_{37}H_{37}D_{18}MoN_3$: C, 67.75; H, 8.45; N, 6.41. Found: C, 67.61; H, 8.29; N, 6.72%.

** The reaction to produce **7** was carried out using 1.164 mmol of **6**. *Other data* for **7**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C); δ 6.86 (s, 6 H, C$_6$*H*$_3$Me$_2$, *o*-H), 6.60 (s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 2.22 (s, 18 H, C$_6$H$_3$*Me*$_2$), 1.48 [s, 9 H, C(CD$_3$)$_2$C*H*$_3$] ^{1}H NMR (300 MHz, [^{2}H$_8$]thf, 25 °C); δ 6.38 (sh s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 6.25 (vbr s, 6 H, C$_6$*H*$_3$Me$_2$, *o*-H), 2.04 (sh s, 18 H, C$_6$H$_3$*Me*$_2$), 1.31 [br s, 9 H, C(CD$_3$)$_2$C*H*$_3$]. Anal. Calc. for $C_{37}H_{36}D_{18}KN_3Mo$: C, 64.04; H, 7.84; N, 6.05. Found: C, 64.71; H, 7.59; N, 5.85%.

†† The reaction to produce **8** was carried out using 0.05 mmol of **7**. *Other data* for **8**: ^{1}H NMR (300 MHz, [^{2}H$_8$]thf, 25 °C); δ 6.26 (s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 5.71 (vbr s, 6 H, C$_6$*H*$_3$Me$_2$, *o*-H), 3.58 (m, 12 H, crypt), 3.53 (m, 12 H, crypt), 2.53 (m, 12 H, crypt), 1.92 (s, 18 H, C$_6$H$_3$*Me*$_2$), 1.50 [s, 9 H, C(CD$_3$)$_2$C*H*$_3$].

‡‡ The reaction to produce **9** was carried out using 0.21 mmol of **7**. *Other data* for **9**: ^{1}H NMR (300 MHz, [^{2}H$_8$]thf, 25 °C); δ 6.85 (m, 8 H, crown aryl), 6.60 (s, 3 H, C$_6$*H*$_3$Me$_2$, *p*-H), 5.81 (br s, 6 H, C$_6$*H*$_3$Me$_2$, *o*-H), 3.5–4.1 (m, 16 H, crown methylene), 2.06 (s, 18 H, C$_6$H$_3$*Me*$_2$), 1.36 [s, 9 H, C(CD$_3$)$_2$(C*H*$_3$)]. Anal. Calc. for $C_{65}H_{52}D_{18}KMoN_3O_{10}$: C, 63.44; H, 7.70; N 3.42. Found: C, 62.83; H, 7.72; N, 3.36%.

§§ Details of the X-ray diffraction study of **9**: monoclinic, space group $P2_1/n$, a = 14.094(4), b = 31.815(8), c = 17.589(7) Å, β = 97.60(2)°, U = 7818(4) Å^3, Z = 4; data/parameter ratio = 10.1, R_1 = 0.0829, wR_2 = 0.1650, GOF on F^2 = 1.083; residuals based on $I > 2\sigma(I)$. CCDC 182/596.

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