New Synthetic Pathways in η-Cycloheptatrienyl Molybdenum Chemistry

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The synthesis of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ from $MoCl_5$ provides a convenient route to η-cycloheptatrienylmolybdenum compounds such as $[Mo(\eta\text{-}C_7H_7)LX_2]$ and $[Mo(\eta\text{-}C_7H_7)L_2X]$, where L = tertiary phosphines or acetonitrile and X = halogen, and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$, R = H, Me.

In the last few years we, and others, have studied the chemistry of η-cycloheptatrienyl compounds of the early transition metals.[1–5] This work has shown that, like the $\eta\text{-}C_5H_5$ group, the $\eta\text{-}C_7H_7$ group normally acts as a robust, non-labile ligand. However the latter differs markedly from the η-cyclopentadienyl system since it requires three electrons from the metal centre in the formation of the metal–ligand bond rather than only the single electron required by the $\eta\text{-}C_5H_5$ group.[1] Also, the seven-electron donor $\eta\text{-}C_7H_7$ ring has a larger cone angle (θ = 154°) than the five-electron donor $\eta\text{-}C_5H_5$ ring (θ = 110°). Therefore, the chemistry of the $\eta\text{-}C_7H_7$–metal derivatives should be extensive but significantly different from that of $\eta\text{-}C_5H_5$–metal compounds.

A substantial barrier to the development of η-cycloheptatrienyl–transition metal chemistry has been the difficulty of finding convenient synthetic routes. However, as described in refs. 1–5, considerable progress has been made in this respect. Here we report new and substantially improved routes to η-cycloheptatrienylmolybdenum derivatives.

The key step is the direct synthesis of the compound $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** from $MoCl_5$ in a one-pot reaction. A mixture of molybdenum pentachloride (1.0 g) and sodium amalgam (0.4 g Na in 8 cm^3 of Hg) at −78 °C was treated with an excess of cycloheptatriene in tetrahydrofuran (thf) (2 g in 50 cm^3). The mixture was stirred and allowed to warm to room temperature over 3 h and stirred for a further 2 h. The volatiles were removed under reduced pressure giving a mixture of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** and $[Mo(\eta\text{-}C_7H_8)_2]$ **2** (2 : 3). After mild thermolysis to convert **2** to **1**,[4c] pure $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]$ **1** could be isolated in 55% yield. In a typical larger scale reaction 10 g of $MoCl_5$ gave 4 g of **1** (39%). Previously, **1** was only available by a metal vapour synthesis route.[4c,5a]

The compound **1** is an excellent precursor to half-sandwich derivatives of the $Mo(\eta\text{-}C_7H_7)$ moiety. Treatment of **1** in acetonitrile with iodine gives dark purple crystals of $[Mo(\eta\text{-}C_7H_7)(MeCN)I_2]$ **3**. The MeCN ligand in **3** is highly labile and **3** reacts with PMe_3 or PPh_3 giving $[Mo(\eta\text{-}C_7H_7)(PR_3)I_2]$, R = Me (**4**) or Ph (**5**), respectively. The dibromo analogue of **3**, namely $[Mo(\eta\text{-}C_7H_7)(MeCN)Br_2]$ **6**, is formed by treatment of **1** in acetonitrile with bromine. As expected the MeCN ligand in **6** is labile and, for example, is displaced by diethyl sulfide giving $[Mo(\eta\text{-}C_7H_7)(Et_2S)Br_2]$ **7**.

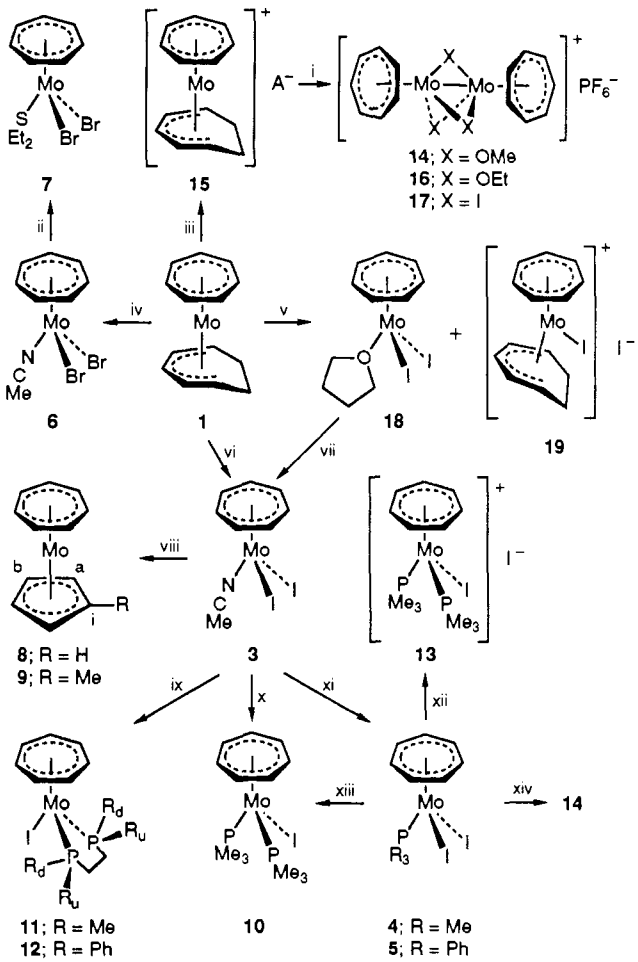
Treatment of **3** with sodium cyclopentadienide or sodium methylcyclopentadienide gives good yields of $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_4R)]$, R = H (**8**) or Me (**9**). The mixed sandwich compound **8** has been previously described but the syntheses gave only low yields.[5a,6]

Reduction of **3** with sodium amalgam in the presence of PMe_3 gives diamagnetic green crystalline $[Mo(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **10** in 82% yield. The related compounds $[Mo(\eta\text{-}C_7H_7)(R_2PCH_2CH_2PR_2)I]$, where R = Me (**11**) or Ph (**12**), are prepared similarly.

Treatment of **4** with excess of PMe_3 affords the cationic paramagnetic compound $[Mo(\eta\text{-}C_7H_7)(PMe_3)_2I][I]$ **13**. Reduction of **4** with $LiAlH_4$ in toluene gives the monoiodide product **10** in 30% yield. The compound **4** also reacts with nucleophiles, for example sodium methoxide, giving the binuclear cation $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}OMe)_3Mo(\eta\text{-}C_7H_7)]^+$ **14**. The compound **1** also provides a route, *via* the cation $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)]^+$ **15**, to the binuclear cations $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta\text{-}C_7H_7)]^+$, where X = OEt (**16**) or I (**17**). The binuclear compounds such as **14**, **16** and **17** have been described previously, but they were only available from lengthy procedures.[7]

Treatment of **1** in tetrahydrofuran with iodine gives $[Mo(\eta\text{-}C_7H_7)(C_4H_8O)I_2]$ **18** and $[Mo(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)I][I]$ **19**. These compounds react with acetonitrile giving **3** in excellent yields. With excess PMe_3, they afford **4** and **13**.

All the new compounds **3–7**, **9–11**, **13**, **15**, **18** and **19** have been characterised by microanalysis and, where appropriate,



Scheme 1 *Reagents*: i, for X = OEt, EtOH, 52%; for X = I, I_2 in thf, 96%; for X = OMe, see xiv; ii, Et_2S in Et_2O, 78%; iii, for A = BF_4, HBF_4 in Et_2O, 62%; for A = PF_6, I_2 in toluene, then NH_4PF_6 in water, 42%; iv, Br_2 in thf, then MeCN, 90%; v, I_2 in thf, 65% **18** and 30% **19**; vi, I_2 in MeCN, 71%; vii, MeCN, quantitative (from **18**), 91% (from **19**); viii, NaC_5H_5 (or NaC_5H_4Me) in thf, 65% (or 85%); ix, Na–Hg and $Ph_2PCH_2CH_2PPh_2$ (or $Me_2PCH_2CH_2PMe_2$) in toluene, 65% (or 61%); x, Na–Hg and PMe_3 in toluene, 82%; xi, for R = Me, PMe_3 in thf, 74%; for R = Ph, PPh_3 in acetone, 85%; xii, PMe_3 in thf, 65%; xiii, $LiAlH_4$ in toluene, 30%; xiv, NaOMe and NH_4PF_6 in MeOH, 55%

by mass, IR, ESR and NMR spectroscopy.† The crystal structure of **18** has been reported previously.[8] The new reactions and the structures proposed are given in Scheme 1.

In conclusion, we have described convenient gram-scale routes to half-sandwich derivatives of the Mo(η-C_7H_7) moiety, many of which will themselves be synthons for the generation of further areas of the chemistry of Mo(η-C_7H_7) derivatives.

† Satisfactory microanalyses have been obtained for all new compounds.

Selected NMR data (solvent [$^2H_6$]benzene): ^1H NMR at 300 MHz, ^{13}C NMR at 75.5 MHz, and ^{31}P NMR at 121.4 MHz; chemical shifts (δ) in ppm and coupling constants in Hz.

9: ^1H NMR δ 4.90 (s, 7 H, η-C_7H_7), 4.80 [t, $J(H_a–H_b)$ 1.8, 2 H, H_a or H_b], 4.66 [t, $J(H_a–H_b)$ 1.8, 2 H, H_a or H_b], 1.75 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR δ 101.7 (C_i), 86.6 (C_a or C_b), 83.7 (C_a or C_b), 80.8 (η-C_7H_7), 14.6 (Me).

10: ^1H NMR δ 4.74 [t, J(H–P) 2.2, 7 H, η-C_7H_7], 1.05 [virtual t, J(H–P) 3.3, 18 H, Me]; $^{13}C\{^1H\}$ NMR δ 86.6 (s, η-C_7H_7), 20.8 [virtual t, J(C–P) 12.1, Me]; $^{31}P\{^1H\}$ NMR δ −24.5 (s, PMe_3).

11: ^1H NMR δ 4.81 [t, J(H–P) 2.2, 7 H, η-C_7H_7], 1.61 [d, J(H–P) 7.9, 6 H, Me_u or Me_d], 1.19–1.34 (m, 2 H, H_u or H_d), 0.78 [d, J(H–P) 7.1, 6 H, Me_u or Me_d], 0.53–0.75 (m, 2 H, H_u or H_d); $^{13}C\{^1H\}$ NMR δ 86.0 (s, η-C_7H_7), 28.4 [virtual t, J(C–P) 20.6, CH_2], 21.7 [virtual t, J(C–P) 14.6, Me_u or Me_d], 15.6 [virtual t, J(C–P) 9.8, Me_u or Me_d]; $^{31}P\{^1H\}$ NMR δ 19.9 (s, $Me_2PCH_2CH_2PMe_2$).

12: ^1H NMR δ 7.88 [t, J(H–H) 8.3, 4 H, Ph], 7.00–7.24 (m, 16 H, Ph), 4.91 [t, J(H–P) 2.1, 7 H, η-C_7H_7], 2.40–2.60 (m, 2 H, H_u or H_d), 1.72–1.96 (m, 2 H, H_u or H_d); $^{13}C\{^1H\}$ NMR δ 141.4 [(d, J(C–P) 27.0, Ph], 127.6–134.8 (Ph), 87.3 (s, η-C_7H_7), 27.2 [virtual t, J(C–P) 19.4, CH_2]; $^{31}P\{^1H\}$ NMR δ 53.5 (s, $Ph_2PCH_2CH_2PPh_2$).

Selected ESR data, **3**: $<g>$ 2.03; A_{iso} 46 G; line width 22 G in MeCN. **4**: $<g>$ 2.06; line width 49 G in thf. **6**: $<g>$ 2.00; A_{iso} 47 G; line width 18 G in MeCN. **13**: $<g>$ 2.05; line width 50 G in CD_3SOCD_3. **15**: $<g>$ 2.00; A_{iso} 42 G; line width 19 G in CD_2Cl_2. **18**: $<g>$ 2.01; A_{iso} 45 G; line width 21 G in thf. 1 G = 10^{-4} T.

Selected mass spectral (electron impact) data, **5**: 441 $(M - PPh_3)^+$.

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