trans-Addition of Two Carbon Substituents across a Benzene Double Bond in [(η⁶-Benzene)Mo(CO)₃]**

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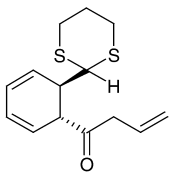
[(Arene)$Cr(CO)_3$] complexes have found widespread application in organic synthesis as a result of the activating and stereodirecting influence of the π Lewis acid fragment $Cr(CO)_3$. The applications include nucleophilic addition to the aromatic ring, to carbonyl and imine functions in side chains, and to configurationally stable benzylic carbocations. Arene lithiation reactions and reactions via benzylic anions also are much more facile in the complex than in the free arene. Diastereoselective and enantioselective variants have been developed for many transformations and they have found application in asymmetric organic synthesis and in the synthesis of chiral ligands for asymmetric catalysis.[1] [(benzene)$Mo(CO)_3$] is readily accessible from $Mo(CO)_6$[2] but, surprisingly, analogous reactions to the ones listed above for the $Cr(CO)_3$ complex have not been reported. Intrigued by this situation, we started a research project on [(arene)Mo$(CO)_3$] complexes and here report the first results.

Thermochemical studies show the arene–Mo bond (68 kcal mol^{-1} in [(η^6-C_6H_6)$Mo(CO)_3$] (**1**)) to be stronger than the arene–Cr bond (53 kcal mol^{-1} in [(η^6-C_6H_6)$Cr(CO)_3$]) (**2**)).[3] M–H bonds are also stronger with the second-row transition metal, as shown by the values of 62 kcal mol^{-1} and 54 kcal mol^{-1} in [$CpMo(CO)_3(H)$] and [$CpCr(CO)_3(H)$], respectively.[4] Kinetically, however, the situation is reversed. The metal–arene bond in **1** is far more labile than that in **2**. This lability and the resulting difficulty in handling the Mo compounds have retarded their use in synthesis. We anticipated that there would be different selectivities in the reactions of the Cr and Mo complexes and that the higher bond strength of the Mo–C and Mo–H bonds would make possible the isolation of intermediates that have eluded characterization in the Cr-mediated reaction sequence. Both of these hypotheses have now been fulfilled.

Addition of 2-lithio-1,3-dithiane[5](**2a**; Scheme 1) to a cold (−78 °C) solution of the benzene–Mo complex **1** in THF*** afforded a yellow precipitate **3a**, which dissolved when the reaction mixture was warmed to −20 °C. The ^{1}H NMR spectrum of **3a** was consistent with that expected for the anionic cyclohexadienyl complex. Treatment of the THF solution of **3a** with allyl bromide (**4a**) produced the [(η^3-allyl)(η^5-cyclohexadienyl)$Mo(CO)_2$] complex (**5a**) which was isolated as a yellow solid. In solution, **5a** is present as a mixture of the two rapidly interconverting *exo–endo* allyl isomers. Analogous reactions with [(η^6-benzene)$Cr(CO)_3$] have been shown previously to give directly the decomplexed cyclohexadiene **6**.[6]



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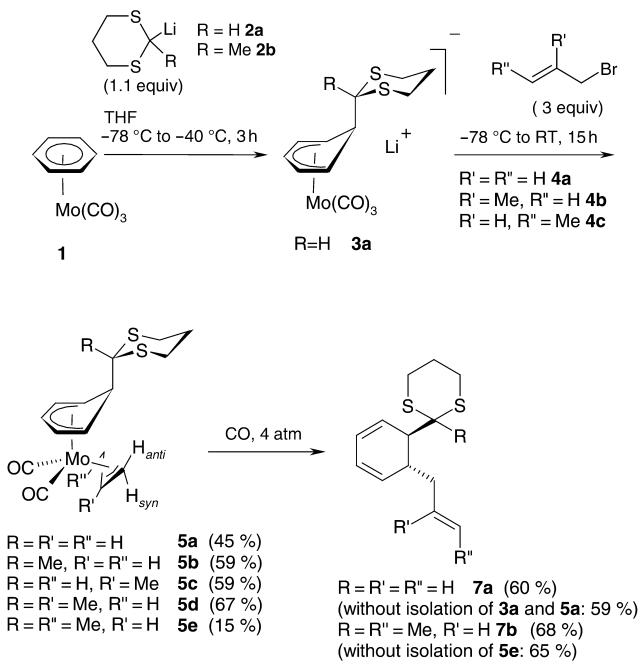
In the Cr-mediated reaction, metal allylation, followed by CO insertion, reductive elimination, and decomplexation occurred readily and intermediates could not be detected. In marked contrast to the above, the Mo–allyl complex **5a** is stable at room temperature. Its intermediacy on the pathway to a *trans*-disubstituted cyclohexadiene was shown by placing a solution of the complex **5a** under 4 atm of CO to give the allyl cyclohexadiene **7a** exclusively (60% yield). No ketone product was observed and this attests to the decreased tendency to carbonylation reactions of the Mo-bound allyl group when compared to Cr-bound groups. Literature precedent to resistance to carbonylation in Mo complexes is exemplified by the report by King et al. that [(η^5-C_5H_5)$MoMe(CO)_3$] does not undergo migratory carbonylation even under 300 atm of CO.[7]

The alkylation/allylation of **1** was then repeated without the isolation of intermediates and with the allylation step carried out under CO pressure. After work-up, **7a** was obtained in 59% yield in this one-pot procedure (see Scheme 1).

Analogous reactions with lithium dithiane and lithium methyldithiane as nucleophiles and allyl and crotyl bromides



Scheme 1. Reaction sequence for formation of **7a**. In situ IR spectroscopic measurements were carried out under conditions designed to optimize the spectra obtained.

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[***] The benzene ligand in **1** is susceptible to substitution by THF at ambient temperature but stable solutions can be prepared by maintaining low temperatures at all times.

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as electrophiles are shown in Scheme 1. The structures of the complexes **5** were deduced from spectroscopic data (IR, NMR) and comparison to closely related complexes such as [CpMo(η^3-*endo*-allyl)(CO)$_2$] and [CpMo(CO)$_2$(η^3-2-methylallyl)].[8] The yield of **5e** was a low 15% because the decomplexed product **7b** was also formed under the reaction conditions and isolated from the mixture in 26% yield. The conditions for reductive elimination thus depend on the substitution pattern of the allyl moiety in the complexes **5**. The 2-methylallyl complex **5c**, exclusively present as the *endo* complex, could not be induced to give the coupled product **7** even under 60 atm pressure of CO. Treatment of **5c** with PPh_3, MeCN, or attempts at oxidation-induced coupling (I_2, air, Ce^{IV}) furnished neither **7** nor the carbonylated product. The structure of the complex **5c** was confirmed by X-ray diffraction (see Figure 1).

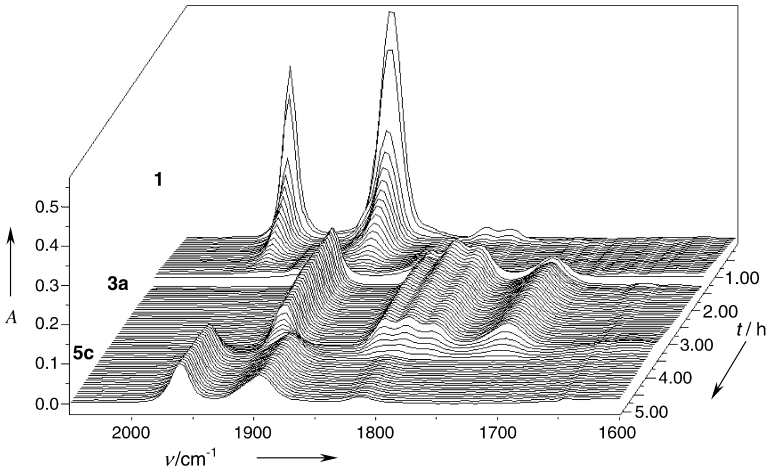

Figure 2. IR stack plot for the sequential reaction of **1** with **2a** and **4b** in THF.

In situ IR spectroscopic measurements[9] were of considerable help in delineating the reaction sequence. Figure 2 shows the sequence for the formation of the complex **5c**.

Complex **1** is characterized by its CO stretching bands at 1969 and 1884 cm^{-1} in the IR spectrum in THF. On addition of **2a** at −78°C (2 equiv), the intensity of these resonances rapidly decreased and after 1 hour at −50°C the ν_{CO} bands of the starting complex **1** had totally disappeared. No new bands were apparent apart from the fleeting appearance of a shoulder at 1899 cm^{-1} and two absorptions at 1803 cm^{-1} and 1783 cm^{-1}. This can be readily explained as the reaction mixture at this stage showed a yellow preciptate. On raising the temperature to 0°C ($t = 1.5$ h), the spectrum of the clear yellow solution now showed $\tilde{\nu}_{CO}$ bands at 1899, 1803, 1783, and 1720 cm^{-1}. These bands are similar to those of the anionic cyclohexadienyl chromium complex previously reported by Semmelhack et al.[10] The pattern of resonances at first appears too complicated for a Mo(CO)$_3$ fragment but it has to be borne in mind that the Li cation coordinates to one of the carbonyl ligands. The band at 1720 cm^{-1} is assigned to the carbonyl ligand bearing the Li cation.[10,11] Addition of allyl bromide at 0°C (at $t = 3.5$ h) brings about the final change to the spectrum with resonances at 1957 and 1891 cm^{-1} assigned to **5c**. In experiments in which methyl allyl bromide (**4b**) was added at −20°C, additional absorptions at 2011, 1965, and 1930 cm^{-1} appeared briefly after the addition of the electrophile. They are tentatively assigned to the η^1-methyl allyl intermediate by comparison with the bands reported for [CpMo(CO)$_3$(η^1-2,4-hexadien-1-yl)] (2015, 1962, 1942 cm^{-1}).[12] Figure 3 shows the decline and growth of the amount of the different species in solution. The experiment illustrates the value of in situ IR spectroscopy for monitoring reactions in real time.

This first study of a sequential nucleophile/electrophile addition sequence to an arene–Mo(CO)$_3$ complex in a nucleophilic/allyl bromide double-addition sequence demonstrates the viability of using π-arene–molybdenum complexes

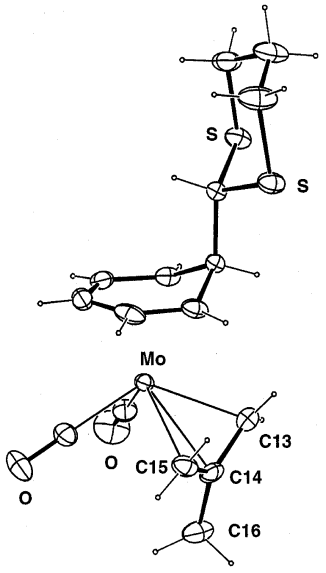

Figure 1. ORTEP view of the X-ray crystal structure of **5c**. Ellipsoids are represented at the 50% probability level. Selected bond lengths [Å] and angles [°] (in brackets for the second molecule of the asymmetric unit): Mo-C13 2.333(3) {2.321(2)}, Mo-C14 2.330(2) {2.320(2)}, Mo-C15 2.322(2) {2.328(2)} , C13-C14 1.415(4) {1.403(4)}, C14-C15 1.398(3) {1.405(4)}, C14-C16 1.514(4) {1.514(4)}; C13-C14-C15 117.4(2) {117.6(2)}, C13-C14-C16 121.3(3) {120.5(3)}, C15-C14-C16 121.1(2) {121.7(3)}.

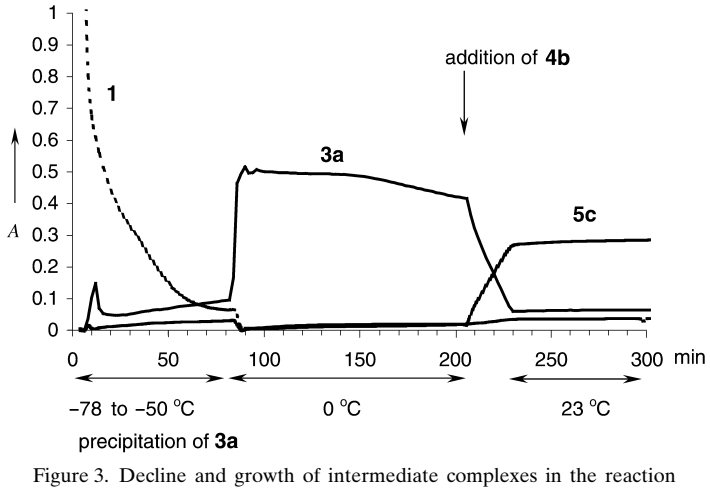

Figure 3. Decline and growth of intermediate complexes in the reaction **1**→**3a**→**5c**.

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in organic synthesis. The reported reactions, the isolation of intermediates, and the final products highlight analogies but also differences between the chromium and molybdenum complexes. These first results are very promising and we predict exciting developments in transition metal-mediated and ultimately catalytic arene transformations by transition-metal–π Lewis acid complexation.

Experimental Section

5c: Under an N_2 atmosphere [(η^6-benzene)Mo(CO)$_3$] (**1**) (250 mg, 0.97 mmol) was added as a solid to cold, freshly distilled, dry, and degassed THF (−78 °C, 5 mL) in a Schlenk reaction vessel. In parallel, a solution of **2a** was prepared by adding *n*BuLi (0.67 mL of a 1.6 M solution in hexanes, 1.07 mmol, 1.1 equiv) to a solution of dithiane (128 mg, 1.07 mmol, 1.1 equiv) in 10 mL of dry THF(−78 to −30 °C, 2 h).[5] After recooling to −78 °C, this solution was transferred rapidly through a Teflon cannula to the solution of the Mo complex at −78 °C. The stirred mixture was allowed to warm to −40 °C over 3 h to give a suspension of a yellow product (complex **3a**). The solution was then recooled to −78 °C and treated with 3-bromo-2-methylpropene (0.30 mL, 2.91 mmol, 3 equiv). The reaction mixture was allowed to warm up to room temperature overnight, and the yellow solution was concentrated to 1 mL. Addition of hexane (10 mL) caused precipitation of a yellow solid which was separated and washed with 3 × 10 mL of hexane to give **5c** (230 mg, 59 %); m.p.: 120–125 °C (decomp.); IR (hexane): $\tilde{\nu}$(CO) = 1970 (vs), 1910 (s); ^{1}H NMR (200 MHz, C_6D_6, 20 °C): δ = 5.27 (t, ^3J(H,H) = 5.5 Hz, 1H; CH), 4.39 (t, ^3J(H,H) = 5.5 Hz, 2H; CH), 3.34 (t, ^3J(H,H) = 5.5 Hz, 2H; CH), 3.13 (d, ^3J(H,H) = 10.0 Hz, 1H; CH), 2.98 (s, 2H; CH_{syn}), 2.52 (dt, ^3J(H,H) = 10.0, 4.6 Hz, 1H; CH), 1.98–2.30 (m, 4H; CH_2), 1.91 (s, 3H; CH_3), 1.83 ppm (s, 2H; CH_{anti}); ^{13}C NMR (75 MHz, C_6D_6, 20 °C): δ = 236.0 (2CO), 108.5 (C quaternary), 98.1 (2CH), 86.3 (CH), 61.8 (2CH), 56.8 (CH), 45.8 (2$C_{terminal}$), 37.7 (CH), 27.6 (2CH_2), 26.2 (CH_2), 24.9 ppm (CH_3); MS: *m*/*z* (%): 287 (13), 231 (16), 161 (55, $C_7H_{13}S_2$), 119 (100, $C_4H_7S_2$), 91 (28); elemental analysis (%) calcd for $C_{16}H_{20}MoO_2S_2$: C 47.52; H 4.98; found: C 47.77; H 5.26.

Crystal structure of **5c:** $(C_{10}H_{13}S_2)(CO)_2(C_4H_7)$; M_r = 404.4; μ = 1.02 mm^{-1}, d_x = 1.579 g cm^{-3}, triclinic, $P\bar{1}$, Z = 4, a = 12.0586(10), b = 12.3014(11), c = 13.1125(11) Å, α = 76.498(10), β = 89.553(10), g = 64.742(10)°, V = 1701.2(3) Å^3; yellow prism 0.14 × 0.17 × 0.31 mm mounted on a quartz fibre with protection oil. Cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å); θ_{max} = 25.8°; 25953 measured reflections, 7571 independent reflections (R_{int} = 0.034) of which 5210 with $|F_o| > 4\sigma(F_o)$; Data were corrected for Lorentz and polarization effects and for absorption ($T_{min,max}$ = 0.8296, 0.9135). The structure was solved by direct methods using SIR97,[13] all other calculations were performed with the XTAL system[14] and ORTEP[15] programs. Full-matrix least-squares refinement based on F using a weight of $1/(\sigma^2(F_o) + 0.0001\,(F_o^2))$ gave the final values R = 0.019, ωR = 0.020, and GOF(F) = 1.00(1) for 499 variables and 5379 contributing reflections. Maximum shift/error = 0.66 × 10^{-3}, max/min residual electron density 0.39/−0.69 e Å^{-3}. Both molecules of the asymmetric unit are similar. CCDC-192276 (**5c**) 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

7a: Allyl bromide (**4a**) (0.131 mL, 1.50 mmol, 3 equiv) was added at −78 °C to a solution of **3a** in THF, prepared as described above starting with **1** (129 mg, 0.50 mmol). The mixture was warmed up to room temperature overnight and then stirred for 12 h under 4 atm of CO. The brown solution was stripped of volatiles under vacuum. The residue was dissolved in hexane and filtered through celite and silica gel. Purification by flash chromatography with cyclohexane/Et_2O (98:2) yielded the cyclohexadiene **7a** as a yellow oil (70 mg, 59 % yield) after evaporation of the solvent. IR (hexane): $\tilde{\nu}$ = 3078 (w), 3038 (m), 2979–2846 (s), 1640 (m), 1462 (s), 1275 (m), 1181 (m), 1099 (m), 1017 (m), 993 (m), 913 (s), 807 (m), 703 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85–5.95 (m, 2H; 2CH), 5.65–5.80 (m, 3H; 3CH), 5.00–5.05 (m, 2H; CH_2), 4.13 (d, ^3J(H,H) = 6.4 Hz, 1H; CH), 2.75–2.85 (*m*, 4H; 2CH_2), 2.65–2.75 (m, 1H; CH), 2.50–2.60 (m, 1H; CH), 1.80–2.20 ppm (m, 4H; 2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT, C-H Correlation): δ = 135.9 (CH), 130.1 (CH), 124.8 (CH), 124.3 (CH), 122.6 (CH), 116.9 (CH_2), 51.8 (CH), 41.5 (CH), 37.8 (CH_2), 34.9 (CH), 30.2, 30.1 (2CH_2), 26.0 ppm (CH_2); MS: *m*/*z* (%): 238 (1.9, M^+), 196 (3, $C_{10}H_{12}S_2$), 119 (100, $C_4H_7S_2$), 91 (49), 77 (21,C_6H_5); HR-MS: calcd for $C_{13}H_{18}S_2$ 238.0821; found 238.0850.

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