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Preliminary communication

Synthesis and photochemical behavior of μ-p-xylene-α,α'-diyldimolybdenum(II) complex

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Summary

Reaction of Na[Mo(cp)(CO)$_3$] (cp = η^5-cyclopentadienyl) with α,α'-dibromo-p-xylene afforded [{Mo(cp)(CO)$_3$}$_2$(μ-CH$_2$C$_6$H$_4$CH$_2$-p)] which reacts with PMe$_2$Ph to give a mono-acyl, and then finally a bis-acyl complex. Photolysis of the μ-p-xylene-α,α'-diyl complex induces homolytic cleavage of the Mo–C bond to produce radical intermediates, which are converted, via p-quinodimethane, to p-xylene and its polymers.

Reaction of α,ω-dihaloalkanes with Na[Mo(cp)(CO)$_3$] does not give dimetallaalkanes, but leads to the formation of cyclic carbenes or metalla-haloalkanes depending on the halide used [1]. We have, however, prepared a dimolybdenaalkane by use of α,α'-dibromo-p-xylene as halide.

α,α'-Dibromo-p-xylene in THF was mixed with a slight excess of Na[Mo(cp)(CO)$_3$] in THF with stirring for 1.5 h at room temperature. The solution was filtered to remove sodium bromide, concentrated in vacuo, and treated with methanol to give yellow crystals of complex **1** in 76% yield.

Complex **1** was characterized by NMR (^{13}C, ^{1}H) and IR spectroscopy as well as molecular weight measurement (found 627 in CH$_2$Cl$_2$ at 35 °C) *. These data are consistent with the structure of **1** (Scheme 1). α,α'-Dibromo-p-xylene, in contrast to

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* Spectroscopic data for [{Mo(cp)(CO)$_3$}$_2$(μ-CH$_2$C$_6$H$_4$CH$_2$-p)] **1**; ^{13}C NMR (in CD$_2$Cl$_2$): δ 5.6 (Mo-CH$_2$-), 94.5 (C$_5$H$_5$), 127.5 (C$_2$ in -C$_6$H$_4$-), 146.8 (C$_{ipso}$ in -C$_6$H$_4$-), 228.8 (CO), 240.8 (CO), ^{1}H NMR (in CD$_2$Cl$_2$): δ 2.94 (Mo-CH$_2$-), 5.22 (C$_5$H$_5$), 7.02 (-C$_6$H$_4$-), IR (Nujol mull): 2000, 1910 cm^{-1} (νCO).

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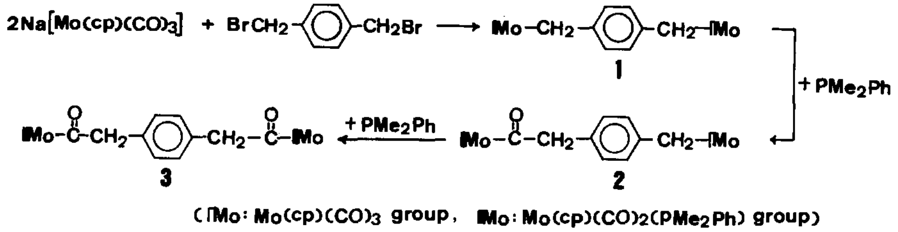

Scheme 1

α,ω-dibromoalkanes, undergoes dimetallation to give a new type of μ-p-xylene-α,α'-diyl complex probably because of its strong electrophilicity. The charge-transfer UV absorption band of **1** is slightly shifted to longer wavelength (λ_{max} 320 nm, $\epsilon = 9607$) as compared with that of $[C_6H_5CH_2Mo(cp)(CO)_3]$ (λ_{max} 314 nm, $\epsilon = 10638$).

Treatment of **1** with PMe_2Ph in THF at room temperature afforded at first the mono-acyl complex **2** and then finally the bis-acyl complex, $[\{Mo(cp)(CO)_2(PMe_2Ph)\}_2(\mu\text{-}COCH_2C_6H_4CH_2CO\text{-}p)]$ (**3**) in 54% yield (Scheme 1). The mono-acyl complex was not isolated pure at this stage. The bis-acyl complex **3** was well characterized by NMR (^{13}C, ^1H, ^{31}P) and IR spectroscopy and molecular weight measurement (found 813.7 in CH_2Cl_2 at 35 °C) *. The *trans*-(CO, CO) structure of **3** was elucidated from ^{13}C NMR data of the CO ligands which show only one signal with J(C–P) 23.9 Hz.

Photochemical behavior of **1** was examined by the spin trapping technique. Figure 1A is the ESR spectrum observed during the irradiation of a benzene solution of **1** with visible light ($\lambda > 420$ nm) in the presence of 2,4,6-tris(t-butyl)nitrosobenzene (TBN) **. This spectrum arises from two radical adducts. The ESR parameters were determined as g 2.0031, a^N 1.492, a^H_m 0.160 mT for the adduct **4**, and g 2.0039, a^N 1.060, a^H_m 0.160 mT for **5**. The satellites observed in both sides of the signals are due to the splitting by $^{95,97}Mo$ isotopes. A hyperfine splitting (hfs) constant a^{Mo} 0.36 mT was obtained.

In an attempt to assign these radical adducts, products of the photolysis of $[Mo_2(cp)_2(CO)_6]$ and $[Mo(CO)_6]$ complexes were examined in the presence of TBN. Radical adducts having the same ESR parameters with those of **4** and **5** were detected during the irradiation of $[Mo_2(cp)_2(CO)_6]$ and TBN system. The irradiation of $[Mo(CO)_6]$ and TBN in benzene gave only the signals of adduct **5**. However, no satellite lines due to Mo isotopes were observed in this spectrum. This strongly implies that **5** has no Mo residue. The ESR parameters of **5** are consistent with those of TBN-t-butylanilino radical ($2,4,6\text{-}(Me_3C)_3C_6H_2NOCMe_3$) within the experimen-

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[*] Spectroscopic data for $[\{Mo(cp)(CO)_2(PMe_2Ph)\}_2(\mu\text{-}COCH_2C_6H_4CH_2CO\text{-}p)]$ 3; ^{13}C NMR (in CD_2Cl_2): δ 20.1 (PMe_2Ph, d, J 33 Hz), 70.9 (Mo-CO-CH_2-), 96.2 (C_5H_5), 238.6 (Mo-CO, d, J 24 Hz), 262.8 (Mo-CO-CH_2-, d, J 12 Hz), ^1H NMR (in CD_2Cl_2): δ 1.93 (PMe_2Ph, d, J 9.0 Hz), 4.18 (Mo-CO-CH_2-), 4.98 (C_5H_5, d, J 1.3 Hz), 6.94 (-C_6H_4-), 7.53 (PMe_2*Ph*, m), ^{31}P NMR (in CD_2Cl_2): δ 32.0 (PMe_2Ph), IR (Nujol mull): 1600 cm^{-1} (νCO, acyl), 1940, 1840 cm^{-1} (νCO, carbonyl).

[**] ESR spectra were measured using a JEOL FE2XG X-band spectrometer (100 kHz field modulation) at room temperature. A degassed sample solution was photolyzed with a high pressure Ushio Hg lamp (500 W) equipped with a glass filter (L-42).

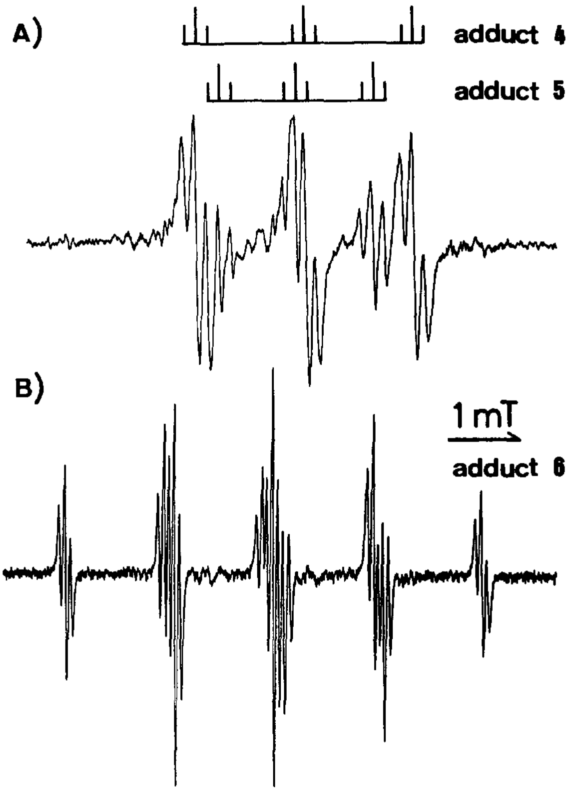
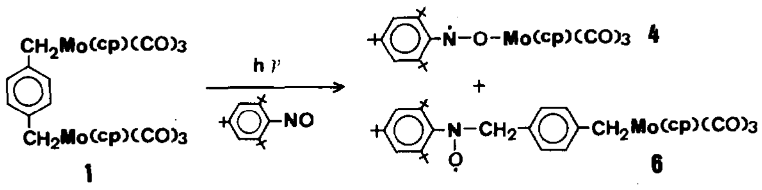


Fig. 1. ESR spectra of a benzene solution of [{Mo(cp)(CO)$_3$}$_2$(μ-CH$_2$C$_6$H$_4$CH$_2$-p)] (1) with added TBN: A) during the irradiation and B) after the irradiation with visible light (λ > 420 nm).

tal error inherent in readings from an ESR spectrum chart [2,3]. The anilino radical adduct was generated by the decomposition of TBN itself by irradiation of the solution containing TBN and the organometallic compounds. It is well known that the photolysis of [Mo$_2$(cp)$_2$(CO)$_6$] produces the metal-centered radical Mo(cp)(CO)$_3$ [4,5], which can be trapped by nitroso compounds [6]. Therefore, we concluded that the adduct **4** is [TBN-Mo(cp)(CO)$_3$]. The g-value suggests that **4** is probably the anilino radical (Scheme 2), in which TBN is bound to the Mo atom through its oxygen atom, rather than the nitroxyl radical [7,8].

When light was cut off in the photolysis of **1**, the intensity of these ESR signals decreased and those due to a new radical adduct **6** appeared (Fig. 1B). The hfs constants a^{N} 1.371, a_{β}^{H} 1.484, and $a_{\mathrm{m}}^{\mathrm{H}}$ 0.08 mT and the g-value 2.0059 are similar to those of TBN-benzyl adduct [3]. When the sample solution was photolyzed once again, the signals due to adduct **6** diminished and those of **4** and **5** were observed. These phenomena are mainly due to the thermal instability of **4** and the photosensitivity of **6**. Prolonged irradiation induced the decrease in the signal intensity of these radical adducts.

Whether the Mo(cp)(CO)$_3$ moiety remains in **6** is not certain from the ESR spectrum, since the hfs due to this moiety might not be observable, because of its remote location from the unpaired electron. However, the adduct **6** is probably the



Scheme 2

nitroxyl adduct, [TBN-$CH_2C_6H_4CH_2$-Mo(cp)$(CO)_3$] because of its sensitivity to visible light. (The radical adduct, TBN-$CH_2C_6H_5$ is stable towards the irradiation of visible light.) It can be seen that photochemical reaction of **1** proceeds stepwise to generate carbon- and metal-centered radicals, which are trapped by TBN (Scheme 2).

On the other hand, *p*-xylene, polymer products and [$Mo_2(cp)_2(CO)_6$] were observed by ^1H NMR measurement of the photolysis product of **1** in C_6D_6 without a spin-trapping agent at room temperature. These ESR and NMR studies clearly show that the excitation of the charge-transfer band of **1** induces homolytic cleavage of the Mo–C bond to produce the radical intermediates and then *p*-quinodimethane. We also synthesized *o*- and *m*-isomers and examined their chemical and photochemical behavior. The spin-trapping technique also provides evidence for photolytic homolysis of the Mo–C bond in these complexes. Details will be reported elsewhere.

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