Carbon Monoxide Transfer to a Metal Co-ordinated Carbyne Ligand: *X*-Ray Crystal Structure of $[Mn_2\{\mu\text{-}C(CO)C_6H_4\text{-}Me\text{-}p\}(CO)_6(\eta\text{-}C_5H_5)]\cdot 0{\cdot}5Et_2O$

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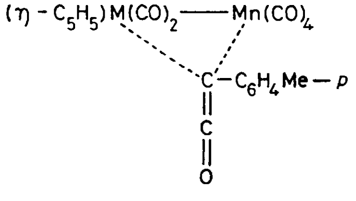
Summary The mononuclear cationic carbyne complexes $[M{\equiv}C{\cdot}C_6H_4Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]BF_4$ (M = Mn or Re) react with $[(Ph_3P)_2N][Mn(CO)_5]$ to give compounds $[MMn\{\mu\text{-}C(CO){\cdot}C_6H_4Me\text{-}p\}(CO)_6(\eta\text{-}C_5H_5)]{\cdot}0{\cdot}5Et_2O$ in which a CO ligand has transferred to the bridging group; the structure of the dimanganese compound has been established by *X*-ray crystallography.

EARLIER we showed that d^{10} metal complexes readily react with metal–carbyne complexes to give products with heteronuclear metal–metal bonds and bridging alkylidyne ligands.[1] By extending these studies to d^8 metal complexes, in order to ascertain whether these species are sufficiently nucleophilic to attack an electrophilic carbyne centre, we have observed a novel reaction between the cationic complexes $[M{\equiv}C{\cdot}C_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]^+$ (M = Mn or Re)[2] and the anion $[Mn(CO)_5]^-$.†

Addition of $[(Ph_3P)_2N][Mn(CO)_5]$ to $[Re{\equiv}C{\cdot}C_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]BF_4$ in CH_2Cl_2 at room temperature affords (40% yield) orange–yellow crystals, from diethyl ether, of a compound analysing for $[MnRe(C{\cdot}C_6H_4\text{-}Me\text{-}p)(CO)_7\text{-}(\eta\text{-}C_5H_5)]{\cdot}\frac{1}{2}Et_2O$ (**1**), m.p. 73 °C (decomp.), ν_{CO} (cyclohexane 2 079m, 2 033s, 2 001s, 1 967s, 1 955m, 1 944m, and 1 878m cm^{-1}; ^1H n.m.r. ($CDCl_3$): τ, 2·66 and 2·84 [AB pattern, 4 H, C_6H_4, *J*(HH) 8 Hz], 4·66 (s, 5 H, C_5H_5), 6·48 [q, 2 H, $CH_2(Et_2O)$, *J*(HH) 6 Hz], 7·64 (s, 3 H, $CH_3{\cdot}C_6$), and 8·79 [t, 3 H, $Me(Et_2O)$, *J*(HH) 6 Hz]. The ^{13}C (^1H-decoupled) n.m.r. spectrum of (**1**) ($CDCl_3$, −40 °C) revealed six metal-bonded CO ligand resonances [202·8 and 200·6 (ReCO), 219·9, 217·6, 214·1, and 211·4 (MnCO) p.p.m.], but no signal in the region (*ca.* 300 p.p.m.) expected for a dimetal bridging carbyne ligand.[1] Moreover, the resonance at 315 p.p.m. of the carbyne–carbon ligand in the spectrum of the reactant $[Re{\equiv}C{\cdot}C_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]BF_4$ was absent in the spectrum of (**1**). Reaction of $[(Ph_3P)_2N]\text{-}[Mn(CO)_5]$ with $[Mn{\equiv}C{\cdot}C_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]BCl_4$ gave (55% yield) red crystals, from diethyl ether, of a compound



(1) M = Re
(2) M = Mn

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† The new reaction described in this communication was reported by one of us (F. G. A. S.) at the Tenth Sheffield International Symposium on Organometallic and Inorganic Chemistry (July 1979), and subsequently at the Ninth International Conference on Organometallic Chemistry (Dijon), September 1979. E. O. Fischer and his co-workers have independently discovered the reaction described herein, and have characterised $[(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(CO)(Ph)\}Re(CO)_4]$ by *X*-ray crystallography (E. O. Fischer, Opening Lecture, Ninth International Conference on Organometallic Chemistry).

$[Mn_2(C{\cdot}C_6H_4\text{-}Me\text{-}p)(CO)_7(\eta\text{-}C_5H_5)]{\cdot}\frac{1}{2}Et_2O$ (**2**), m.p. 80 °C (decomp.), ν_{CO} (cyclohexane) 2 075m, 2 020s, 1 994s, 1 970s, 1 961s, 1 948m, and 1 850m cm^{-1}. The ^1H n.m.r. spectrum of (**2**) showed the expected resonances for the groups present, and the ^{13}C n.m.r. spectrum was very similar to that of (**1**). Since complexes (**1**) and (**2**) were of a new type, a single crystal *X*-ray diffraction study was carried out on (**2**).‡

Crystal data: $C_{20}H_{12}O_7Mn_2{\cdot}\frac{1}{2}C_4H_{10}O$, *M* 511·3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8{\cdot}189(3)$, $b = 18{\cdot}077(9)$, $c = 7{\cdot}638(4)$ Å, $\alpha = 95{\cdot}66(4)$, $\beta = 106{\cdot}30(3)$, $\gamma = 85{\cdot}47(3)°$, $U = 1078{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}50$, $D_c = 1{\cdot}58$ g cm^{-3}, $F(000) = 518$, $\mu(\text{Mo-}K_\alpha) = 12{\cdot}8$ cm^{-1}. Current *R* 0·039 (*R'* 0·040) for 2 505 intensities $[2{\cdot}9 \leqslant 2\theta \leqslant 50°, I \geqslant 2{\cdot}5\sigma(I)$. Syntex $P2_1$ diffractometer, Mo-K_α ($\lambda = 0{\cdot}71\ 069$ Å)].

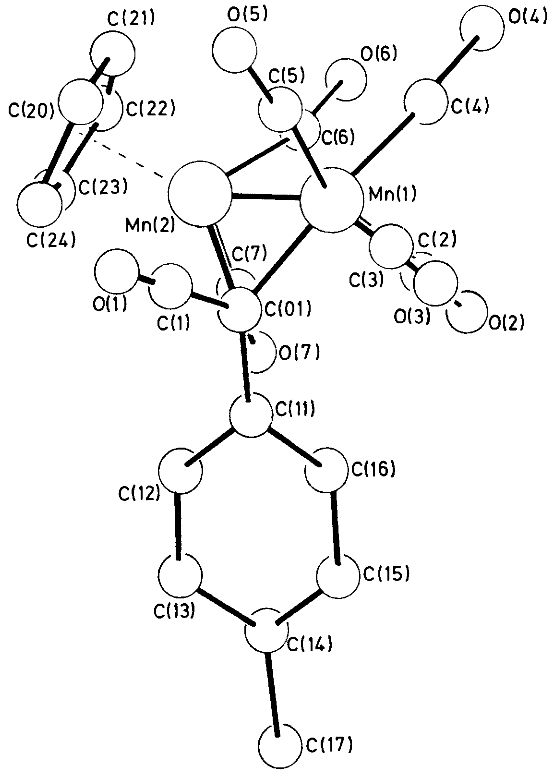

FIGURE. Molecular structure of $[Mn_2\{\mu\text{-}C(C_6H_4\text{-}Me\text{-}p)CO\}(CO)_6(\eta\text{-}C_5H_5)]$.

The molecular structure (Figure) shows a manganese–manganese bond {2·735(1) Å, similar in length to that found [2·779(1) Å] in $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_4Me)_2]$[3]} symmetrically bridged by the ligated carbon atom of the original carbyne group [Mn(1)–C(01) = Mn(2)–C(01) = 2·128(4) Å]. All Mn–C–O groups are essentially linear except for Mn(2)·C(6)·0(6) [161·5(4)°] which displays semi-bridging character.[4]

A unique feature of the structure is the presence of the C(1)O(1) group bonded to C(01), with C(1)–O(1) = 1·167(5) Å, and C(01)–C(1) = 1·326(6) Å. The former distance could correspond either to a C≡O or a C=O linkage.[5] The latter distance, however, suggests C=C character so that the μ-$C(C_6H_4Me)CO$ group might be better regarded as a one-electron keten bridge $[C(C_6H_4Me){=}C{=}O]$ rather than a three-electron ylide bridge $[\overset{-}{C}(C_6H_4Me)\text{-}\overset{+}{C}{=}O]$ across the metal–metal bond. Either canonical form leads to a diamagnetic complex. Evidently formation of (**1**) and (**2**) involves transfer of a CO group from $Mn(CO)_5$ to a metal–carbyne centre, a process which may be involved in some catalytic reactions of carbon monoxide.

Establishment of the structure of (**2**), and by analogy that of (**1**) also, enables the spectroscopic properties to be understood. I.r. bands of (**1**) and (**2**) at 1 878 and 1 850 cm^{-1}, respectively, may be assigned to the carbonyl of the μ-$C(CO)C_6H_4Me$ groups. In addition to the resonances of the six metal-bonded CO ligands, the ^{13}C n.m.r. spectrum of (**1**) has a band at 162·1 p.p.m., and that of (**2**) a band at 163·4 p.p.m. These signals are due to the non-metal bonded *C*O group, as was demonstrated by ^{13}CO studies. In an enriched sample of (**2**) the Mn–*C*O ligand resonances greatly increased in intensity, while the band at 163.4 p.p.m. was also stronger, relative to the η-C_5H_5 peak (89·5 p.p.m.).

The results described herein, involving carbonyl–carbyne reactions at a dimetal system, are probably related to the formation of $[(OC)_4(Me_3P)Cr\{\mu\text{-}C(CO_2Me)Ph\}Pt(PMe_3)_2]$ from $[(OC)_4(Me_3P)Cr(\mu\text{-}C{\cdot}Ph)Pt(PMe_3)_2]^+$ and methoxide ion.[6] Also relevant is the work of Hermann *et al.*,[7] and Kreissl *et al.*,[8] on keten formation at a mononuclear metal centre *via* interaction of CO with carbenes and carbynes, respectively.

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‡ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1979, 42.

[2] The complexes $[M{\equiv}CPh(CO)_2(\eta\text{-}C_5H_5)]BCl_4$ (M = Mn or Re) were discovered by E. O. Fischer and his co-workers (E. O. Fischer, E. W. Meincke, and F. R. Kreissl, *Chem. Ber.*, 1977, **110**, 1140; E. O. Fischer, R. L. Clough, and P. Stückler, *J. Organometallic Chem.*, 1976, **120**, C6), but in the chemistry described herein we prefer to employ the related cations $[M{\equiv}C{\cdot}C_6H_4\text{-}Me\text{-}p\text{-}(CO)_2(\eta\text{-}C_5H_5)]^+$.

[3] M. Creswick, I. Bernal, and W. A. Hermann, *J. Organometallic Chem.*, 1979, **172**, C39.

[4] R. J. Klingler, W. M. Butler, and M. D. Curtis, *J. Amer. Chem. Soc.*, 1978, **100**, 5034.

[5] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

[6] J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *J.C.S. Chem. Comm.*, following communication.

[7] W. A. Herrmann, J. Plank, M. L. Zeigler, and K. Weidenhammer, *J. Amer. Chem. Soc.*, 1979, **101**, 3133; W. A. Herrmann and J. Plank, *Angew. Chem. Internat. Edn.*, 1978, **17**, 525.

[8] F. R. Kriessl, W. Uedelhoven, and K. Eberl, *Angew. Chem. Internat. Edn.*, 1978, **17**, 859; F. R. Kreissl, K. Eberl, and W. Uedelhoven, *ibid.*, 1978, **17**, 860; IX International Conference on Organometallic Chemistry (Dijon), Abstracts paper B9.