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Preliminary communication

KINETIC CHARACTERISTICS OF THE FOUR-ELECTRON BRIDGING CARBONYL

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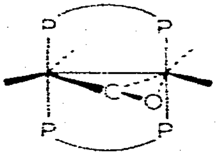
Summary

The structure of $Mn_2(CO)_5(dpm)_2$ (dpm = $Ph_2PCH_2PPh_2$) is discussed and by NMR spectroscopy it is shown to have a four-electron bridging carbonyl group.

There is substantial interest in the idea that certain structural units may confer substitution lability and possibly even catalytic reactivity upon a molecule. The *trans*-effect is the classic example of ligand effects, now followed by the "*cis*-effect" [1]. Unusual reactivity has been demonstrated for the multiple metal—metal bonds in $(C_5H_5)_2Mo_2(CO)_4$ [2] and $H_2Os_3(CO)_{10}$ [3]. π to σ interconversions of π-allyl complexes, and bending of linear nitrosyls are further transformations which may produce "active sites".

A recent report by Colton, Commons and Hoskins [4] has added a new feature to the structural chemistry of μ_2-carbonyl bridges [5]. Their communication showed $Mn_2(CO)_5(dpm)_2$ (dpm = $Ph_2PCH_2PPh_2$) to be a metal—metal bonded dimer (I) containing four terminal carbonyls and a fifth carbonyl which bridges the two metals in a unique fashion: one metal atom forms a normal two-electron MnC dative bond* while the other metal bonds to the C≡O bond as it would to a heteroolefin. Coordinative saturation obtains if this unique carbonyl is considered to function as a four-electron donor. The heteroolefin component of this four-electron bridging carbonyl (4EBC) might be expected to be labile. Examples of NO, CN^- and N_2 bound "sideways" are unknown. π-bound nitrile ligands are controversial [6]. π-bound ketones are known only as one component of hetero-



(I)

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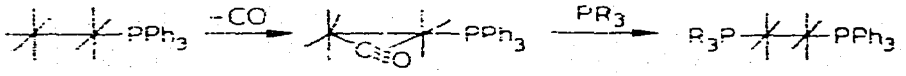
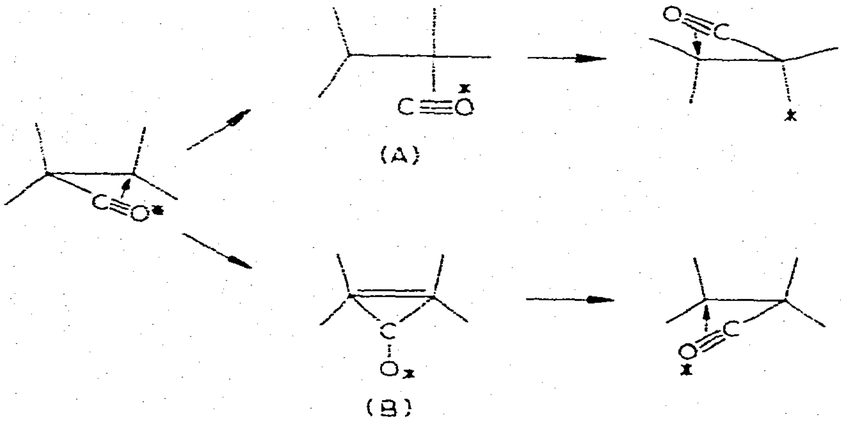
[*] A π component may of course accompany this σ bond.

diene ligands [7]. If I could be shown to have a thermally accessible isomer in which the 4EBC had reverted to a two-electron bonding mode, small molecules might find ready access to one or even two metal atoms. The potential for subsequent catalyzed transformations is apparent. Atwood and Brown [8] have suggested that the 4EBC may participate in *cis*-activated substitution of CO by phosphine in $Mn_2(CO)_9(PPh_3)$ (eq. 1). We describe here some results pertinent to this question.



(1)

The ^{31}P NMR spectrum of I provides information on the rate of rearrangements (eq. 2 and 3).



(2)

(3)

With complete proton decoupling at –80°C (Fig. 1), an AA'XX' pattern is evident*. This is consistent with the structure in the crystal; since the inner coordination sphere has only a plane of symmetry, the two phosphorus nuclei attached to one metal remain distinct from those on the second. On raising the temperature to 30°C, no intramolecular rearrangement is evident**. Decomposition occurs at higher temperatures. Rearrangement modes 2 and 3 in which the bridge ligand reverts to a two-electron donor mode (A or B), are thus undetectable by NMR. On the basis of observed linewidths, the free energy of activation for such a process must exceed 15.6 kcal/mol***.

Chemical evidence suggests unusual reactivity for the 4EBC. Compound I appears to be the terminal step in substitution on $Mn_2(CO)_{10}$ with dpm. It is stable to refluxing decalin. We have isolated $Mn_2(CO)_6(dpm)_2$ (II) at an early stage in the reaction and established its intermediacy by converting it to I on further heating in hydrocarbon solvents. The hexacarbonyl could be any of the isomeric forms C—E.

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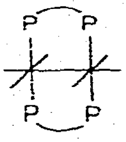
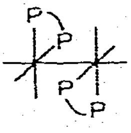
*Spectral parameters: δ(A) 75.9 ppm, δ(B) 59.5 ppm, J(AA') 110 Hz, J(AB) 100 Hz, J(AB') ≈ 5 Hz. It is significant that the coupling constant through the CH_2 bridge is as large as the *trans* coupling constant (through Mn).

**The quadrupolar manganese nuclei cause some broadening, however.

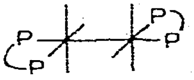
***When this work was complete, a full report on I noted "a single, slightly broadened resonance at 69.45 ppm downfield from H_3PO_4." [9].



(C)



(D)



(E)

Isomer E is excluded by the observation of a ^{31}P NMR singlet at +70.2 ppm (−84°C in CH_2Cl_2). The carbonyl frequencies of $Mn_2(CO)_6(dpm)_2$ (1995 w, 1920 s, 1870 m in CH_2Cl_2) closely resemble those of *mer,trans*-$Mn(CO)_3(PR_3)_2X$ monomers, and are distinct from those of *fac,cis*-$Mn(CO)_3(PR_3)_2X$ species. Thus, *fac,cis*-$MnBr(CO)_3(dpm)$ (configuration determined by observation of a ^{31}P NMR singlet at +12.7 ppm in CH_2Cl_2 at 30°C) has ν(CO) frequencies of 2025(s), 1955(m) and 1920(s). We therefore assign structure C to $Mn_2(CO)_6(dpm)_2$**.

With the bridging phosphine chelates already established in II, the transformation of II into I is precisely the process envisioned by Atwood and Brown (eq. 1). We find that it is also possible to effect the reverse reaction. At 25°C carbonylation of I occurs slowly at 1 atm CO or rapidly under 3—5 atm (Fig. 1). The4EBC

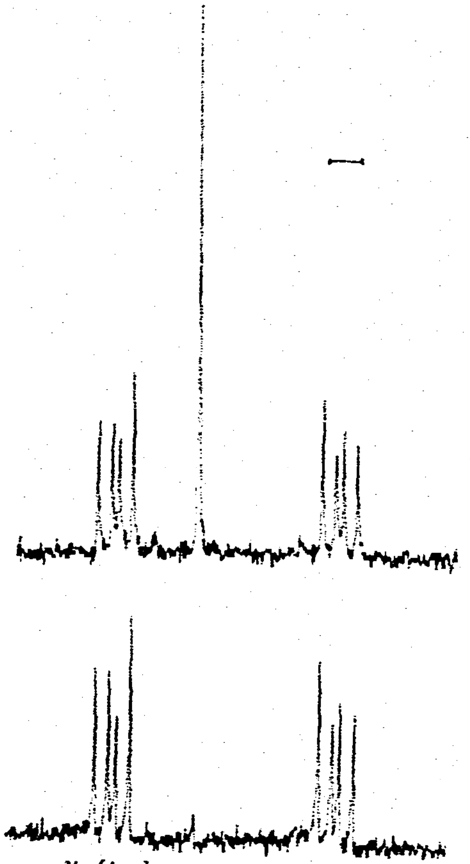


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of (a) $Mn_2(CO)_5(dpm)_2$ in CH_2Cl_2 at −80°C (lower) and (b) $Mn_2(CO)_5(dpm)_2$, treated with 1 atm CO for 12 h, in CH_2Cl_2 at −80°C (upper); the singlet due to $Mn_2(CO)_6(dpm)_2$ appears at 70.2 ppm. Calibration bar indicates 100 Hz.

[**] This contradicts an earlier assignment, based on chemical evidence (bromination reaction) [10].

thus forms the structural basis for reversible carbon monoxide transport, a feature it shares with $H_2Os_3(CO)_{10}$ and $Cp_2Mo_2(CO)_4$.

Acknowledgment

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