ether by the usual line width technique. The approximate activation enthalpies shown in Table I are similar to the 15–20 kcal/mol generally observed for ligand exchange from cation solvation shells[22–24] and larger than the 6–10 kcal/mol measured for proton exchange, for instance, in aqueous methylammonium ion,[25] $AlCl_3$,[24,26] and imidazolium ion[27] solutions.

Similar pmr spectral measurements have been possible for other systems, including acetic acid, diethylamine, and pyridines, and attempts are being made to expand this list still further.

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A New Aromatic Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes[1]

Sir:

We have discovered a new type of metalated derivative formed in the reaction of $Ph_2\overline{P\text{-}C_6H_4\text{-}M}n(CO)_4$ (**1**)[2] with *cis*-$CH_3M(CO)_4L$ (M = Mn, L = PPh_3, **2**; M = Mn, L = CO, **3a**; M = Re, L = CO, **3b**). A solution of **1** (0.10 g, 0.23 mmol) and **2** (0.20 g, 0.45 mmol) in toluene (5 ml) is refluxed under nitrogen for 2 hr during which time the latter reagent is consumed as monitored by ir absorptions in the carbonyl-stretching region. The solvent is removed by water aspirator and the solids are redissolved in hexane for chromatography (silica gel, 20 mm diameter column, ×40 cm). Elution first with hexane and then with increasing quantities of added benzene up to 25% by volume reveals six bands of which the second proves to be a yellow-orange substance, air-stable in the solid, recrystallized from ether–hexane at −20°, $C_{44}H_{28}Mn_2O_8P_2$ (**4**).[3] The yield varies from 15 to 25% (based on **2**) depending on the reaction conditions.[4] The other products obtained are discussed below.

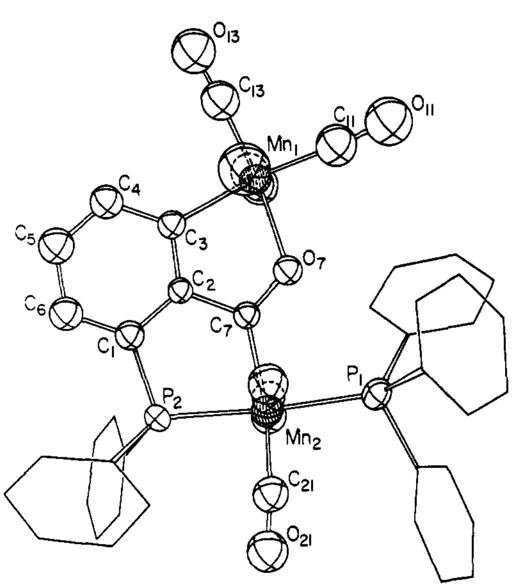

Figure 1. The structure of $\overline{Ph_2P\text{-}[C_6H_3(\overline{CO})(Mn(CO)_4)]\text{-}M}n\text{-}(CO)_3PPh_3$ (**4**) projected onto the plane defined by Mn(1), Mn(2), and P(2). There are two axial CO groups, one above and one below each of the two Mn atoms, appearing greatly foreshortened in the present perspective. The bond angles and distances are within expected limits. Some selected values are given as follows: C(3)–Mn(1), 2.03 Å; Mn(1)–O(7), 2.05 Å; O(7)–C(7), 1.27 Å; C(7)–Mn(2), 2.03 Å; C(3)–Mn(1)–O(7), 80°; C(2)–C(7)–O(7), 112°; P(2)–Mn(2)–C(7), 82°.

A set of X-ray diffraction data was collected for a suitable crystal of **4**[5] on a Syntex P$\bar{1}$ automated diffractometer using graphite monochromated Mo Kα radiation. A θ–2θ scan was employed at a programmed rate varying from 2.4 to 24 deg/min from the weakest to the strongest reflections. Lorentz and polarization corrections were applied but no absorption corrections were required for the crystal of the dimension 0.18 × 0.22 × 0.24 mm for which the maximum effect on F due to absorption is ±3.5% (μ = 8 cm^{-1}). The structure was solved by the standard Patterson, Fourier, and difference-Fourier techniques. All 56 nonhydrogen atoms have been located. Least-squares refinement (in which thermal parameters for manganese and phosphorus were allowed to refine anisotropically) has resulted in a discrepancy index of R = 7.0% for 2518 independent nonzero reflections. Refinement is continuing.

The structure is shown in Figure 1. The coordination geometry around the manganese atoms is near-octahedral while that around the phosphorus atoms is tetrahedral. All of the labeled atoms form an extended coplanar system in which the deviation from the

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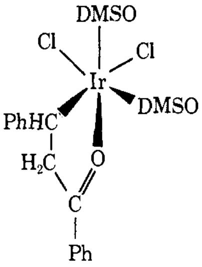
[3] *Anal.* (Heather King, UCLA) Calcd: C, 61.68; H, 3.29. Found: C, 61.65; H, 3.46. Mass spectrum: Parent ion obsd *m/e* 856 (calcd 856). The first significant fragmentation ion at *m/e* 772 showing loss of three CO's followed by fragmentation ion peaks showing loss of four through eight CO's. Ir, metal carbonyl absorptions (hexane) (cm^{-1}): 2074 (m), 2024 (w), 1992 (vs), 1984 (s, shoulder), 1946 (vs), 1935 (vs), 1926 (shoulder).

[4] The formation of the new metalation product is favored in concentrated solution and in some cases optimized in the reaction of the molten solids at 140–150°.

[5] Crystals of **4** were found to belong to the centrosymmetric monoclinic space group $C2/c$ ($2/m$, no. 15), Z = 8. Unit cell data are a = 10.763 (2) Å, b = 34.713 (5) Å, c = 21.479 (3) Å, β = 92.93 (1)°, and V = 8014 Å^3; ρ_{obsd} = 1.44, ρ_{calcd} = 1.42.

least-squares plane is less than 0.05 Å. Pertinent bond angles and distances are cited in the caption to Figure 1. The acyl group C(7)O(7) is coordinated through oxygen to Mn(1), similar to metal coordination of acyl groups observed in two previously reported structures, **5** (DMSO = dimethyl sulfoxide)[6] and **6**.[7] In the latter, the C=O and O→Mn bond distances of 1.23 and 2.06 (7) Å, respectively, compare favorably with the analogous parameters in **4** (see Figure 1). Metal-coordinated acyl groups have also been postulated in a number of other derivatives where their presence is associated with a characteristic band in the region 1495–1550 cm^{-1}.[8] Accordingly, in the ir spectrum of **4** we observe a strong absorption at 1460 cm^{-1} (surrounded by bands of lower intensity due to absorptions of the phenyl rings).



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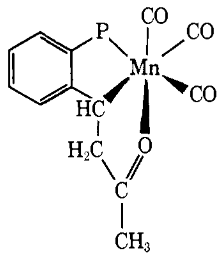

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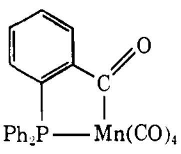
The other substances obtained in the reaction between **2** and **1** are as follows. The first band in the chromatographic separation proved to be **1**, either unreacted or formed by intramolecular metalation of **2** in competition with its reaction with **1** (or both). Under conditions in which the yield of **4** is optimized, approximately 25% of the initial weight of **1** is recovered. The third band is an orange compound, $C_{41}H_{28}Mn_2O_5P_2$ (**7**)[9] (yield 15–30%), formed by the loss of three CO groups from **4**. This transformation has been separately demonstrated by heating **4** to 170° where melting and gas evolution take place to form **7** essentially exclusively. This also accounts for the weakness of the ion peaks resulting from the loss of the first and second CO molecules in the mass spectrum of **4**.[3] The fourth band is another orange compound, $C_{61}H_{43}Mn_2O_7P_3$ (**8**), of low volatility obtained in 5–40% yield. It is analogous to **4** with a carbonyl on Mn(1) replaced by PPh_3. Both **7** and **8** display a strong absorption (1470 and 1460 cm^{-1}, respectively) indicating the presence of a metal-coordinated acyl group. The fifth and sixth chromatographic bands correspond to minor amounts (1–4% each) of compounds $Ph_2\overline{PC_6H_4Mn}(CO)_3L$ (**9**) and $\overline{Ph_2PC_6H_4C(O)Mn}(CO)_4$[2b] (**10**) which are also separately obtained in the treatment of **1** with Ph_3P or CO, respectively. The acyl group absorption for **10** is observed at 1610 cm^{-1}.

In the reaction of **1** with **3a**, we obtain $C_{27}H_{13}O_9PMn_2$ (**11**),[9] an analog of **4** in which $Ph_3P(1)$ is replaced by CO. This is accompanied by only trace amounts of the other derivatives in the reaction of **1** with **2** and also by $Mn_2(CO)_{10}$ (anywhere from 5 to 40% based on **3a**). Such decomposition is completely avoided using methylrhenium pentacarbonyl (**3b**) which results in **12**, an analog of **11** in which one of the two Mn atoms (as yet undetermined) is replaced by Re.



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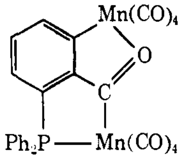

11

Repeating the above reactions with L = $P(p\text{-}FC_6H_4)_3$ or $P(p\text{-}CH_3C_6H_4)_3$ leads to analogous compounds; the rate of metalation for the tolyl rings is higher by about 25% while that for the fluoro-substituted rings is decreased by a similar amount compared to that observed for the phenyl groups, similar to what is found for the intramolecular aromatic metalation reaction.[10] A number of rearrangements must also accompany such substitution in order to account for the observed products. This is presently under investigation. The metalation reaction may also be extended to complexes of other transition metals containing aromatic rings activated by intramolecular metalation.[10]

Acknowledgment. We wish to thank the UCLA Computing Center for intramural support of a portion of the computing expenses in this work and Mr. Irwin Poliakoff for experimental assistance.

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[11] Publication No. 3075.

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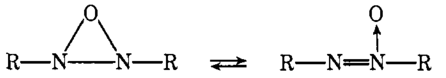
Thiadiaziridine 1,1-Dioxides. An Unusually Stable Strained Heterocyclic Ring System

Sir:

The literature on three-membered rings containing varying numbers of heteroatoms is extensive.[1] They present synthetic challenges and their chemistry is theoretically intriguing. To date, however, only one such ring system comprised entirely of heteroatomic units has been isolated and characterized.[1c,2] Oxadiaziridines are somewhat labile reverting to their valence isomers, azoxyalkanes (eq 1), at room temperature with half-lives of hours.[1c]



1 **2** (1)

We wish to report the second example (**4a,b**) of a three-membered heteroatomic ring system. These substituted thiadiaziridine dioxides were postulated as intermediates by Ohme,[3,4] Schmitz,[3] and Preuschhof[4]

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