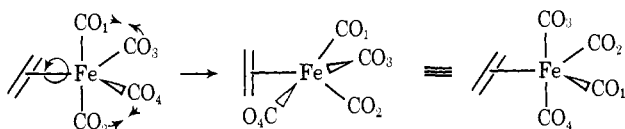


perature, independent of solvent, and unaffected by added free olefin, unequivocally rules out simple olefin rotation as being solely responsible for the averaging of the carbonyl groups, since such a process would not exchange axial carbonyl groups with equatorial ones as demanded by the observed single line at high temperatures. Unfortunately, due to the simplicity of the spectrum, the nmr line shape changes contain no mechanistic information. As a result analysis of the axial-equatorial carbonyl group exchange in terms of "basic permutational sets"<sup>12</sup> with the present data is not feasible. We would only like to point out that a synchronous olefin rotation and Berry rearrangement of the carbonyl groups (Scheme I), which by the way are

Scheme I



inseparable, provides a simple pathway for the exchange process.<sup>13</sup> The process is also attractive since it offers a ready rationale for the observed dramatic increase in the activation barrier upon the replacement of one CO group by an olefin moiety.<sup>3a</sup> Should the above process be operative it also suggests a very close correspondence between the strength of the metal olefin bond, or more precisely its  $\pi$  component,<sup>15,16</sup> and the obtained energies of activation based on carbonyl group exchange.<sup>17</sup> Our observation that the rate of rearrangement decreases in the series styrene<sup>-18</sup> > (ethyl acrylate)- > benzalacetone- > (diethyl maleate)-  $\sim$  (diethyl fumarate)- > trifluoroethylene-Fe(CO)<sub>4</sub><sup>19</sup> is a clear indication of this.

Studies are in progress to establish more convincingly the correlation between Fe-olefin bond strength and activation barriers for carbonyl group exchange.

**Acknowledgment.** We thank the University of Alberta and the National Research Council of Canada for financial support of this research.

(12) P. Meakin, E. Muetterties, and J. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(13) We note that Whitesides and Mitchell<sup>14</sup> have established that the rearrangement in (CH<sub>3</sub>)<sub>2</sub>NPF<sub>4</sub> is consistent with the Berry mechanism.

(14) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

(15) The  $\sigma$  component of the metal-olefin bond by virtue of its cylindrical symmetry contributes little to the barrier for olefin rotation. The  $\pi$  interaction between metal d orbitals and  $\pi^*$  olefin orbitals is, however, different for the olefin in the equatorial plane and perpendicular to it. The barrier to olefin rotation will therefore primarily reflect the differences in the  $\pi$  interactions between these two forms.

(16) We thank a referee for bringing this point to our attention.

(17) In fact, the activation energies obtained are not a true measure of the barriers to olefin rotation, since if we assume, as we have done, the Berry rearrangement in these complexes then the geometry of the transition state is close to a square pyramid with the olefin occupying the apical position. The barrier to olefin rotation in this state is greatly reduced compared to that in the ground state because of the fourfold character of the barrier.

(18) Limiting spectrum at 148°K, four carbonyl resonances in the ratio 1:1:1:1.

(19) Limiting spectrum at 283°K, three carbonyl resonances in the ratio 2:1:1 (<sup>19</sup>F decoupled), and single broad resonance at 338°K.

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## Preparation and Structure of $\eta^1$ -Pentachlorocyclopentadienylpentacarbonylmanganese(I), $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$

Sir:

In this communication the preparation and structure of the first  $\sigma$ -bonded pentachlorocyclopentadienyl-transition metal complex are described. The preparation of pentachlorocyclopentadienyl-metal complexes has proved a somewhat difficult task in the past. Decachloroferrocene and decachlororuthenocene were obtained by repetitive metalation exchange-halogenation reactions.<sup>1,2</sup> Bis- and monopentachlorocyclopentadienyl (C<sub>5</sub>Cl<sub>5</sub><sup>-</sup>) complexes of mercury have been prepared with 1,2,3,4,5-pentachlorocyclopentadiene or thermally unstable TIC<sub>5</sub>Cl<sub>5</sub>.<sup>3,4</sup> We recently reported the convenient synthesis of halogen substituted  $\eta^5$ -cyclopentadienylrhodium complexes *via* the insertion reactions of diazocyclopentadienes into halogen-bridged dirhodium species.<sup>5</sup> Extension of this reaction has resulted in the first C<sub>5</sub>Cl<sub>5</sub><sup>-</sup> derivatives of manganese.<sup>6</sup>

Two yellow crystalline products,  $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$  (I) and  $(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3\text{Mn}$  (II) are obtained from the reaction of manganese pentacarbonyl chloride and 2,3,4,5-tetrachlorodiazocyclopentadiene in pentane at room temperature. They are conveniently separated by fractional crystallization from the filtered reaction mixture.<sup>7</sup> Four carbonyl stretching bands are observed in the solution (cyclohexane) infrared spectrum of the less soluble compound I. These occur at 2128 (m), 2077 (w), 2044 (vs), and 2011 (s) cm<sup>-1</sup> and are assigned to the A<sub>1</sub><sup>(2)</sup>, B<sub>1</sub>, E, and A<sub>1</sub><sup>(1)</sup> modes, respectively.<sup>8</sup> Excluding bands due to the carbonyl groups, the remainder of the spectrum (400-400 cm<sup>-1</sup>; Nujol mull) is virtually identical with that reported for Hg(C<sub>5</sub>Cl<sub>5</sub>)<sub>2</sub>,<sup>3,4</sup> indicating that the pentachlorocyclopentadienyl ligand is  $\sigma$ -bonded. This has been confirmed by the preliminary results of an X-ray structural analysis which are reported at this time.

Crystals of  $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$  are monoclinic: space group  $P2_1/n$ , a special setting of  $P2_1/c$  (no. 14,  $C2_h^5$ );  $a = 13.701$  (2),  $b = 8.758$  (1),  $c = 13.329$  (1) Å;  $\beta = 107.78^\circ$  (1);  $Z = 4$ . Data collection (Nb-filtered Mo K $\alpha$  radiation, Syntex P<sub>1</sub> Autodiffractometer) yielded 1560 symmetry independent reflections having  $2\theta_{\text{MoK}\alpha} < 43.0^\circ$  (0.5 limiting Cu K $\alpha$  spheres) and  $I > 2\sigma(I)$ . Direct methods were used to locate the manganese and three chlorine atoms. The remaining atoms were located using standard difference-Fourier techniques. Unit-weighted full-matrix least-squares refinement, employing anisotropic thermal parameters for all atoms,

(1) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **92**, 3239 (1970).

(2) F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **95**, 870 (1973).

(3) G. Wulfsberg and R. West, *J. Amer. Chem. Soc.*, **93**, 4085 (1971).

(4) G. Wulfsberg, R. West, and V. N. Mallikarjuna Rao, *J. Amer. Chem. Soc.*, **95**, 8658 (1973).

(5) V. W. Day, B. R. Stults, K. J. Reimer, and A. Shaver, *J. Amer. Chem. Soc.*, **96**, 1227 (1974).

(6) While this work was in progress, a possible C<sub>5</sub>Cl<sub>5</sub><sup>-</sup> complex of palladium was briefly mentioned by N. Yoshimura, S.-I. Murahashi, and I. Moritani, *J. Organometal. Chem.*, **52**, C58 (1973).

(7) A standard reaction of 24-hr duration, employing 0.45 g of each reactant in 20 ml of pentane, yields 0.32 g of I and 0.29 g of II. Satisfactory analysis has been obtained for both compounds.

(8) Theory predicts three infrared bands for local C<sub>4v</sub> symmetry but the infrared-forbidden B<sub>1</sub> mode is sometimes observed: L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969), and references therein.

has resulted in a conventional unweighted residual,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , of 0.041. The crystal used for data collection gave slightly more than one-half copper sphere of data before the six standard reflections being monitored every 300 reflections showed a sharp decrease in intensity, presumably due to a rapid degradation of the compound. The remaining intensity measurements necessary for a complete set of  $\theta$ - $2\theta$  scan data (at least to  $2\theta_{\text{MoK}\alpha} = 55^\circ$ ) will be made on other crystals of this compound and then merged with the present data set. The additional data will be necessary if we are to make the best possible comparisons between the structural parameters of this complex and others in a series containing halogen substituted cyclopentadienyl groups.

$(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$  is composed of discrete molecules in which the manganese atom achieves a filled valence shell configuration by bonding octahedrally to five carbonyl groups and a  $\sigma$ -bonded pentachlorocyclopentadienyl ligand (Figure 1). The  $\text{C}_5\text{Cl}_5^-$  group is bonded to the manganese atom through a single carbon atom at a distance of 2.204 (6) Å and possesses the normal characteristics of a  $\sigma$ -bonded cyclopentadienyl group, namely two short, 1.351 (8, 6, 6)<sup>9</sup> Å, and three long, 1.487 (8, 12, 13) Å, carbon-carbon bonds. The four carbon atoms of the cyclopentadienyl ring involved in the two double bonds are bonded to chlorine atoms at an average distance of 1.693 (6, 4, 5) Å, while the fifth carbon atom is bonded to a chlorine atom at a distance of 1.798 (6) Å—observations also consistent with a  $\sigma$ -bonded cyclopentadienyl ring. The four carbonyl groups, whose carbon atoms form a quasi-square oriented approximately normal to the Mn-CP1 vector, have average manganese-carbon bond lengths of 1.871 (8, 10, 21) Å, while the group trans to the pentachlorocyclopentadienyl group has a manganese-carbon bond of 1.833 (8) Å. The carbonyl groups are bonded linearly to the manganese (average Mn-C-O angle of 177.2 (8, 6, 14)<sup>o</sup>) and have average values of 1.151 (8, 4, 7) Å for the carbon-oxygen distances.

Compound I is stable in the solid state. Samples exposed to light or air show no visible signs of deterioration. It melts, with effervescence, at 110° to give quantitative yields of II. This conversion also takes place slowly in solution at room temperature and may account for the isolation of II from the original reaction mixture.

When II is the sole product desired, the insertion reaction is carried out in octane. After 24 hr at room temperature, the reaction solution is warmed to ~80° for a few minutes, cooled, and stripped to dryness. Sublimation of the residue yields II uncontaminated by I. The infrared spectrum (cyclohexane solution) of II in the carbonyl stretching region shows two bands at 2050 (s) and 1982 (vs)  $\text{cm}^{-1}$  assigned to the  $A_1$  and E modes, respectively. These are shifted an average of 28  $\text{cm}^{-1}$  to higher wave numbers than those observed for  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5\text{Mn}$ . This suggests that the  $\eta^5\text{-C}_5\text{Cl}_5$  ring is a poorer electron donor and/or better electron acceptor than the  $\eta^5\text{-C}_5\text{H}_5$  moiety. The solid state spectrum of II, excluding carbonyl related vibrations, has fewer bands than that of compound I and is

(9) The first number in parentheses is the rms estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.

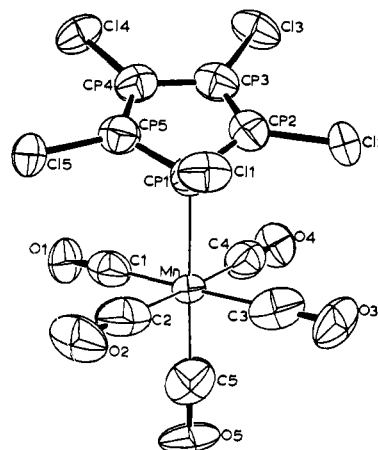


Figure 1. The molecular structure of  $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$ .

similar to that reported for  $\text{Fe}(\text{C}_5\text{Cl}_5)_2$ .<sup>1</sup> This is expected for  $\eta^5$  coordination of the pentachlorocyclopentadienyl group.<sup>10</sup>

The relative stability of  $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$  is notable, as  $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_5\text{Mn}$  is not known. This may be due to the decreased nucleophilicity of  $\text{C}_5\text{Cl}_5^-$ <sup>11</sup> relative to  $\text{C}_5\text{H}_5^-$  so that displacement of two carbonyl groups is less readily achieved. Also, the well-known ability of halogens to stabilize metal-carbon  $\sigma$ -bonds<sup>12</sup> probably contributes to the stability of I.<sup>13</sup>

Investigation of the chemical properties of these complexes is currently in progress.

**Acknowledgment.** The advice and interest of Professor H. C. Clark, in whose laboratories the preparative work was conducted, are gratefully acknowledged.

(10) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(11) R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

(12) M. L. H. Green in "Organometallic Compounds," Vol. II, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968.

(13) When  $(\eta^5\text{-C}_5\text{H}_5\text{Cl})(\text{CO})_5\text{Mn}$  and  $[\eta^5\text{-C}_5(\text{C}_6\text{H}_4)\text{Cl}](\text{CO})_5\text{Mn}$  were prepared *via* reaction of the appropriate diazocyclopentadienes, no evidence was found for stable  $\eta^1$  derivatives.<sup>14</sup> This emphasizes the importance of both factors.

(14) K. J. Reimer, unpublished observations.

(15) Ontario Graduate Fellow, 1973-1974.

(16) National Research Council of Canada Postdoctorate Fellow, 1972-1974.

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## Iodo- and Hydridotantalum(III) Complexes of Dialkylacetylenes

Sir:

The isolation and study of stable transition metal complexes of monoolefins and acetylenes and their derivatives have provided insight into transition metal catalyzed reactions of these hydrocarbons. Heretofore most of these studies have been restricted to systems involving olefins or acetylenes which are activated by electronegative substituents;<sup>1</sup> with relatively few ex-

(1) See, for example, A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972); J. Schwartz, D. W. Hart, and J. L. Holden, *ibid.*, **94**, 9269 (1972).