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Insertion Reactions of Diazoindene with some Rhodium and Manganese Halides

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Diazoindene inserts into the rhodium–chlorine bond in $[CODRhCl]_2$, where COD = 1,5-cyclooctadiene, to give $(\eta^5$-1-$C_9H_6Cl)RhCOD$. Similar complexes could not be isolated from $[Rh(CO)_2Cl]_2$ and $[Rh(CO)(PPh_3)Cl]_2$. This was attributed to the labilizing ability of the indenyl ring and the absence of a chelating ligand. The complexes $Mn(CO)_5X$, where X = Cl, Br and I, react with diazoindene to give $(\eta^5$-1-$C_9H_6X)Mn(CO)_3$. Only the pentahapto *bonding mode was observed for the indenyl ligand. The reactions of complexes of the type $Mn(CO)_{5-n}L_nX$, where L = phosphine or phosphite, X = Cl or Br, and n = 1 or 2, were investigated.* Cis-*$Mn(CO)_4PPh_3Br$ loses a carbonyl and the phosphine to give $(\eta^5$-1-$C_9H_6Br)Mn(CO)_3$.*

Introduction

Interest in indenyl complexes has always been high due to the complementary nature of this ligand with respect to the parent cyclopentadienyl group. Thus, *monohapto*-indenyl ligands have proved useful in elucidating the mechanisms of rearrangement of main group cyclopentadienyls [1]. Recently, a *trihapto* bonding mode, often postulated but rarely seen for the cyclopentadienyl ligand, was established for an indenyl group in the complex (η^5-indenyl)(η^3-indenyl)$W(CO)_2$ [2]. In addition, the indenyl ligand can be more useful synthetically than C_5H_5 by virtue of its ability to slip from *penta*- to *trihapto* in certain systems such as (η^5-indenyl)RhAB, where A and B are neutral ligands, thus permitting S_N-2 ligand substitution reactions to proceed [3].

The latter complexes are of interest as precursors to chiral organometallic materials which our laboratory has begun to study [4]. Treatment with alkyl halides, RX, should, by analogy to the cyclopentadienyl complexes [5], give compounds of the type (η^5-indenyl)RhABR·X which are chiral. Moreover study of the reactions of these oxidative addition products should provide interesting information on the stereochemical rules that govern this system. To do this a stereochemical probe is needed. Unsymmetrically substituted cyclopentadienyl ligands have proved to be useful in the study of chiral cyclopentadienyliron systems [6]. Indenyl ligands, monosubstituted at the carbon adjacent to the benzene ring (*i.e.*, C_1), appear to be promising candidates to supply such an unsymmetrical ring.

Earlier work has shown that diazocyclopentadiene inserts into the Rh–Cl bond of various dimers to give complexes of the type $(\eta^5$-$C_5H_4Cl)RhA_2$ [7]. It was decided to investigate the insertion chemistry of 1-diazoindene to see: *1*) if a range of potentially useful halosubstituted indenyl complexes was available and *2*) if the halide atom was on C_1 thus imparting asymmetry to the group. Since diazocyclopentadiene also inserts into the Mn–X bond of $Mn(CO)_5X$ [7] the analogous reactions between 1-diazoindene and various complexes of the type $Mn(CO)_{5-n}L_nX$, where L = PPh_3 and $P(OPh)_3$, X = Cl, Br and n = 0, 1 or 2, have also been studied.

Experimental

Synthesis of all organometallics was carried out under nitrogen using inert atmosphere techniques [8]. Tetrahydrofuran was freshly distilled from sodium-benzophenone. Chromatography was done on activated alumina, 80–200 mesh (Anachemia). Infrared spectra were taken on a Perkin Elmer 257 spectrophotometer and were calibrated with polystyrene (1601 cm^{-1}). NMR spectra were performed on a Varian T60A spectrometer with TMS as internal standard. Elemental analysis was performed by Midwest Microlab Ltd., Indiana and Guelph Chemical Laboratories Ltd., Ontario. High resolution mass spectra were measured on an AEI-MS-902 spectrometer at Cornell University.

$Mn_2(CO)_{10}$ (Pressure Chemicals) was purified by sublimation at 85 °C/0.3 mm Hg. PPh_3 (Aldrich)

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was recrystallized from MeOH, while $P(OPh)_3$ (Strem) and Cl_2 (Matheson) were used without further purification, as were *p*-toluenesulfonylchloride (Anachemia) and sodium azide (Alfa Products). Indene (Aldrich) was distilled before use.

The following compounds were prepared using published procedures: $Mn(CO)_5X$ (X = Cl, Br, I) [9], *cis*-$Mn(CO)_4LX$ (L = PPh_3, $P(OPh)_3$; X = Cl, Br) [10], $Mn_2(CO)_8(PPh_3)_2$ [11], *trans*-$Mn(CO)_4PPh_3Br$ [12], *mer*-$Mn(CO)_3[P(OPh_3]_2X$ (X = Cl, Br) [13], $[RhCODCl]_2$ (COD = 1,5-cyclooctadiene) [14], and p-$CH_3C_6H_4SO_2N_3$ [15].

Diazoindene ($C_9H_6N_2$)

The procedure of Rewicki and Tuchscherer [16] was modified in the following manner. Diethylamine (17.6 ml, 12.4 g, 0.17 mol) was added to a 0 °C solution of indene (20.1 ml, 20.0 g, 0.17 mol) and *p*-toluenesulfonylazide (33.5 g, 0.17 mol) in a 250 ml round-bottomed flask. The reaction flask was sealed and the mixture allowed to stand at 0 °C for 6 days. At that time, the decrease in intensity of the N≡N stretch at 2123 cm^{-1} (hexane) in the infrared spectrum indicated 50% reaction. Additional diethylamine (17.6 ml) and indene (20.0 ml) were added and the mixture was allowed to stand at 0 °C for 4 days. The absence of the azide peak indicated complete reaction. The mixture was poured into water (400 ml), hexane (600 ml) was added and the contents were transferred to a separatory funnel. The hexane layer was extracted with water until the washings were no longer basic. The solution was dried over Na_2SO_4 and concentrated to half volume. The solution was cooled at −20 °C overnight causing precipitation of N,N-diethyl-p-toluenesulfonamide (16.0 g, 20% of the total azide). The mother liquor was stripped to a deep red liquid from which excess indene was distilled (23 °C, 0.4 mm Hg, pot temperature 45 °C). The residue was transferred to a 25 ml volumetric flask and diluted to the mark with hexane. The solution was standardized by reacting a 2 ml aliquot with PPh_3 (2.6 g, 0.01 mol) in ether to give dark red crystals of C_9H_6–N=N–PPh_3 [17] (1.9 g, m.p. 153–156 °C). Yield: 2.4 *M* diazoindene solution, 8.4 g (34%). IR (hexane) ν(N≡N): 2071 cm^{-1}.

Caution: Although diazoindene can be distilled, explosions result if any unreacted azide is present in the crude product [16]. In view of the explosive instability of diazocyclopentadiene [18, 19] we recommend that diazoindene always be kept in solution.

fac-*Tricarbonylchlorobis(triphenylphosphite)manganese(I)*, fac-*$Mn(CO)_3Cl[P(OPh)_3]_2$*

The method is a modification of that of Angelici *et al.* [13], $Mn(CO)_5Cl$ (0.20 g, 0.86 mol) was dissolved in 20 ml $CHCl_3$ in a three-necked round-bottomed flask equipped with a nitrogen inlet and a dropping funnel. $P(OPh)_3$ (1.9 ml, 1.6 g, 5.12 mol) was added dropwise and the reaction was stirred overnight at room temperature. Hexane (60 ml) was added and the solution concentrated in a stream of N_2 to 10 ml volume to give a yellow precipitate. The mother liquor was removed with a syringe and the precipitate recrystallized from $CHCl_3$/hexane; yield, 0.41 g (60%) yellow crystals. IR ($CHCl_3$) ν(CO): 2067 (s), 2007 (vs), 1955 (vs) cm^{-1}, (the *mer* isomer, IR ($CHCl_3$) ν(CO): 2082 (w), 2008 (vs), 1960 (s) cm^{-1} [13]).

fac-*Tricarbonylbromobis(triphenylphosphite)manganese(I)*, fac-*$Mn(CO)_3Br[P(OPh)_3]_2$*

This was prepared in an analogous fashion with the reaction time being 6 days at room temperature; yield, 70%. IR ($CHCl_3$) ν(CO): 2066 (s), 2008 (vs), 1960 (vs) cm^{-1} (the *mer* isomer, IR ($CHCl_3$) ν(CO): 2089 (w), 2008 (vs), 1966 (s) cm^{-1}).

η^5-1-Chloroindenyl-1,5-cyclooctadienerhodium(I), $Rh(1,5\text{-}C_8H_{12})(\eta^5\text{-}1\text{-}C_9H_6Cl)$

$[CODRhCl]_2$ (0.5 g, 1.0 mmol) was suspended in 50 ml hexane in a 100 ml three-necked round-bottomed flask and 2.3 ml of a 2.5 *M* solution of diazoindene (2.0 mmol) were added dropwise with stirring. The mixture was stirred for 2 hours, the solvent was stripped and the residue chromatographed, eluting with hexane. The first band (yellow) gave the desired product (η^5-1-C_9H_6Cl)RhCOD as yellow crystals. The second yellow band was unreacted $[CODRhCl]_2$ (0.100 g). The product appeared to be heat and light sensitive. Yield (based on reacted starting material): 11%, m.p. 119–120 °C; NMR ($CDCl_3$): τ 2.83 (m, 4 H), 3.77 (m, 1 H), 4.92 (d, 1 H, J (Rh–H) = 4 Hz), 6.16 (broad d, 4 H, J (Rh–H) = 18 Hz), 8.13 (broad s, 8 H); mass spectrum m/e 360 (M^+, 100%). *Anal.* Calcd for $C_{17}H_{18}ClRh$: C, 56.59; H, 4.99%. Found: C, 55.51; H, 5.05%.

(η^5-1-Haloindenyl)tricarbonylmanganese(I), $Mn(CO)_3(\eta^5\text{-}1\text{-}C_9H_6X)$

$Mn(CO)_5Cl$ (0.300 g, 1.30 mmol) was dissolved in 50 ml THF in a three-necked round-bottomed flask. Diazoindene solution (0.55 ml, 2.36 *M* 1.3 mmol) was added dropwise and the mixture was stirred at room temperature for 24 hours. The solvent was stripped and the residue chromatographed on alumina, eluting with toluene. The single orange band containing (η^1-1-C_9H_6Cl)$Mn(CO)_3$ was stripped and recrystallized from CH_2Cl_2/hexane at −78 °C (oil at room temperature); yield, 73%. IR (hexane) ν(CO): 2028 (s), 1957 (s), 1948 (s) cm^{-1}; NMR ($(CD_3)_2CO$): τ 2.2–3.1 (m, 4 H), 4.6 (ABq, 2H, JH–H = 3 Hz); mass spectrum; m/e calcd for $C_{12}H_6ClMnO_3$: M^+, 287.9386; Found: M^+, 287.9399; fragmentation 288 (M^+, 11%), 260 (M^+

–CO, 9%), 232 (M^+ –2CO, 16%), 204 (M^+ – 3CO, 100%).

(η^5-1-C_9H_6Br)$Mn(CO)_3$ was prepared as above but the reaction mixture was refluxed until the peak in the infrared due to the N_2 group had disappeared (about 6 hours). Orange crystals were obtained after chromatography and recrystallization from CH_2Cl_2/hexane; yield, 57%. IR (hexane) ν(CO): 2028 (s), 1957 (s), 1948 (s) cm^{-1}; NMR ($(CD_3)_2CO$): τ 2.4–3.3 (m, 4 H), 4.4 (d, 2 H); mass spectrum; m/e calcd for $C_{12}H_6BrMnO_3$: M^+, 331.8881; Found: M^+, 331.8872; fragmentation 332 (M^+, 35%), 304 (M^+ –CO, 34%), 276 (M^+ –2CO, 61%), 248 (M^+ –3CO, 100%).

(η^5-1-C_9H_6I)$Mn(CO)_3$ was prepared as above, the reaction being refluxed overnight. Upon chromatography and recrystallization orange crystals were obtained; yield, 35%. IR (hexane) ν(CO): 2028 (s), 1956 (s), 1948 (s) cm^{-1}; NMR ($(CD_3)_2CO$): τ 2.4–3.1 (m, 4 H), 4.5 (d, 2 H); mass spectrum; m/e calcd for $C_{12}H_6IMnO_3$: M^+, 379.8744; Found: M^+, 379.8731; fragmentation 380 (M^+, 12%), 352 (M^+ –CO, 10%), 324 (M^+ –2CO, 17%), 296 (M^+ –3CO, 100%).

Reaction of cis-*Mn(CO)$_4$(PPh$_3$)Br and C$_9$H$_6$N$_2$*

cis-$Mn(CO)_4(PPh_3)Br$ (0.220 g, 0.44 mmol) was dissolved in 50 ml THF in a 100 ml three-necked round bottomed flask and diazoindene solution (0.50 ml, 2.5 *M*, 0.44 mmol) was added dropwise. The solution was refluxed until the peak due to the N_2 group in the infrared was no longer observed (about 4 hours). The solution was stripped to a brown oil and chromatographed. The first band (orange), eluted with toluene/CH_2Cl_2 (1:1), was (η^5-1-C_9H_6Br)$Mn(CO)_3$. No other carbonyl-containing fractions were eluted. Yield, 0.040 g (27% of starting compound).

Reaction of cis-*Mn(CO)$_4$[(OPh)$_3$]Br and C$_9$H$_6$N$_2$*

As above, *cis*-$Mn(CO)_4[P(OPh)_3]Br$ (0.150 g, 0.27 mmol) in 50 ml THF was treated with diazoindene (0.12 ml, 2.3 *M*, 0.27 mmol). The reaction was followed by IR and after stirring for 26 hours at room temperature, the solvent was stripped and the residue chromatographed on alumina, eluting with hexane. The first band was diazoindene (0.038 g). Also present in this eluant were traces of (η^5-1-C_9H_6Br)-$Mn(CO)_3$ identified by its infrared spectrum. The second band, eluted with CH_2Cl_2, gave *mer*-$Mn(CO)_3$-$[P(OPh)_3]_2Br$, identified by its infrared spectrum (0.120 g, 53% based on the starting manganese complex).

Reaction of mer-*Mn(CO)$_3$[P(OPh)$_3$]$_2$Cl and C$_9$H$_6$N$_2$*

mer-$Mn(CO)_3[P(OPh)_3]_2Cl$ (0.130 g, 0.16 mmol, 10% excess) was dissolved in 50 ml THF. Diazoindene solution (0.064 ml, 2.4 *M*, 0.15 mmol) was added dropwise and the reaction stirred for 2 days at room temperature. The solvent was stripped and the orange-brown residue chromatographed with hexane. The first band (0.020 g) was a mixture of unreacted diazoindene and (η^5-1-C_9H_6Cl)$Mn(CO)_3$. Traces of (η^5-1-C_9H_6Cl)$Mn(CO)_2[P(OPh)_3]$ were eluted with hexane/CH_2Cl_2 (9:1) and identified by its infrared spectrum. The third band, eluted with hexane/CH_2Cl_2 (3:1), was the starting *mer* compound (0.070 g, 53.8% of starting compound) contaminated by traces of the *fac* isomer (~7% by infrared spectrum).

Reaction of fac-*Mn(CO)$_3$[P(OPh)$_3$]$_2$Cl and C$_9$H$_6$N$_2$*

fac-$Mn(CO)_3[P(OPh)_3]_2Cl$ (0.200 g, 0.25 mmol) and diazoindene solution (0.097 ml, 0.23 mmol) were combined in a similar manner for 1 day. Upon chromatography of the residue, infrared analysis indicated the first band contained trace amounts of $C_9H_6N_2$ and (η^5-1-C_9H_6Cl)$Mn(CO)_3$, the second band contained traces of (η^5-1-C_9H_6Cl)$Mn(CO)_2$-$[P(OPh)_3]$ and the third was identified as *mer*-$Mn(CO)_3[P(OPh)_3]_2Cl$ (0.060 g, 30.0% isomerization of the *fac* isomer).

Reaction of mer-*Mn(CO)$_3$[P(OPh)$_3$]$_2$Br and C$_9$H$_6$N$_2$*

mer-$Mn(CO)_3[P(OPh)_3]_2Br$ (0.150 g, 0.18 mmol) and diazoindene solution (0.068 ml, 0.16 mmol) were stirred in THF for 4 days. After chromatography and infrared analysis, the first band was found to contain traces of $C_9H_6N_2$ and (η^5-1-C_9H_6Br)-$Mn(CO)_3$, the second traces of (η^5-1-C_9H_6Br)Mn-$(CO)_2[P(OPh)_3]$ and the third contained the starting *mer*-$Mn(CO)_3[P(OPh)_3]_2Br$ (0.075 g, 50% of starting material). A fourth band, eluted with 1:1 hexane: CH_2Cl_2, was identified as *fac*-$Mn(CO)_3[P(OPh)_3]_2Br$ (0.015 g, 10% isomerization of the *mer*-).

Reaction of fac-*Mn(CO)$_3$[P(OPh)$_3$]$_2$Br and C$_9$H$_6$N$_2$*

fac-$Mn(CO)_3[P(OPh)_3]_2Br$ (0.200 g, 0.24 mmol) and diazoindene solution (0.089 ml, 0.21 mmol) were reacted for 3 days. When chromatographed, the first band contained traces of diazoindene and (η^5-1-C_9H_6Br)$Mn(CO)_2$, the second traces of (η^5-1-C_9H_6Br)$Mn(CO)_2[P(OPh)_3]$, the third was *mer*-$Mn(CO)_3[P(OPh)_3]_2Br$ (0.050 g, 25% isomerization of the *fac*-), and the fourth, *fac*-$Mn(CO)_3[P(OPh)_3]_2$-Br (0.030 g, 15% recovery).

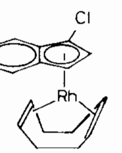
Results and Discussion

Treatment of $[CODRhCl]_2$ with diazoindene gave yellow crystals of (η^5-1-C_9H_6Cl)RhCOD. The presence of two resonances in the proton NMR of the five-membered ring is consistent only with structure A with the chlorine atom positioned on the carbon

TABLE I. Infrared Data.

Complex[a]	$\nu(CO)$[b]		
$(\eta^5\text{-}C_9H_7)Mn(CO)_3$[c]	2030	1949	1940
$(\eta^5\text{-}C_9H_6Cl)Mn(CO)_3$	2028	1957	1948
$(\eta^5\text{-}C_9H_6Br)Mn(CO)_3$	2028	1957	1948
$(\eta^5\text{-}C_9H_6I)Mn(CO)_3$	2028	1956	1948
$(\eta^5\text{-}C_5H_5)Mn(CO)_2P(OPh)_3$[d]	1970	1909	
$(\eta^5\text{-}C_9H_6Cl)Mn(CO)_2P(OPh)_3$	1989	1928	
$(\eta^5\text{-}C_9H_6Br)Mn(CO)_9P(OPh)_3$	1986	1924	

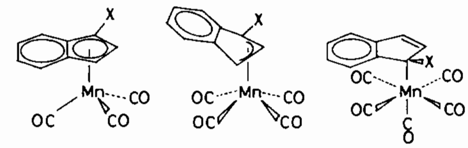
[a]In hexane. [b]In cm^{-1}. [c]In cyclohexane, ref. 23. [d]In cyclohexane, ref. 24.



A

adjacent to the benzene ring (the carbon to which the diazo group was originally attached). Thus, an unsymmetric prochiral ligand has been prepared *via* this insertion reaction. Unfortunately, the reactions of $[Rh(CO)_2Cl]_2$ and $[RhCO(PPh_3)Cl]_2$ did not yield the desired complexes but led instead to total decomposition of the rhodium starting materials. Perhaps the labilizing ability of the indenyl ligand, [*i.e.*, η^5-18 electron complex $\rightarrow$ η^3-16 electron complex] in the presence of weak ligands such as unreacted diazoindene [20] leads to the loss of CO and the formation of unstable complexes. The chelating nature of the diolefin ligand may prevent the decomposition in the case of $[\eta^5\text{-}1\text{-}C_9H_6Cl]$-RhCOD. It is notable that $[Rh(CO)_2Cl]_2$ reacts with $Ph_4C_5N_2$ to give $(\eta^5\text{-}C_5Ph_4Cl)Rh(CO)_2$ where the η^5-Cp ligand does not have special labilizing tendencies [7b].

Treatment of the complexes $Mn(CO)_5X$, where X = Cl, Br, I, leads to the isolation of $(\eta^5\text{-}1\text{-}C_9H_6\text{-}X)Mn(CO)_3$*. Here again the ^1H NMR clearly establishes the position of the halogen atom as shown in B. This assignment is confirmed by the report of the X-ray analysis of the bromo-complex [22]. The infrared spectrum in the carbonyl region shows a small shift to higher wave numbers upon substituting halogen for hydrogen on the indenyl ligand (Table I). The production of simple *pentahapto* derivatives is noteworthy in view of previous results



B C D

obtained with diazocyclopentadiene and diazotetrachlorocyclopentadiene.

In the former case, the simple *pentahapto* complexes $(\eta^5\text{-}C_5H_4X)Mn(CO)_3$ are formed [7b]. However, with the latter reactant the *monohapto* complexes $(\eta^1\text{-}C_5Cl_4X)Mn(CO)_5$, where X = Cl, Br, are first formed and can be isolated [7a]. Gentle heating causes the loss of two CO ligands and the conversion from the *monohapto* to the *pentahapto* bonding mode. It was concluded that a predissociation of $Mn(CO)_5X$ to $Mn(CO)_4X$ provided the coordination position to which the diazo ligand attached. Insertion could then occur to give *monohapto* species which in the case of C_5H_4X were too unstable with respect to loss of two CO ligands but which with C_5Cl_4X were stable due to the reduced nucleophilicity of the ring. It is reasonable to apply the same reasoning to the reactions of diazoindene with these complexes. Thus the *monohapto* complex D would be the first product expected. In view of the results with C_5H_4X this structure is expected to be unstable. Loss of one CO ligand would lead to a *trihapto* complex C. In the case of C_5H_4X such a bonding mode is also not expected to be stable and was not seen in the C_5Cl_5 case either. However, the indenyl ligand's ability to exist in the *trihapto* mode is well characterized [25]. In addition, the presence of the halogen atom might reduce the nucleophilicity of the ligand thus favouring less involvement with the metal as was seen with the $\eta^1\text{-}C_5Cl_5$ ligand. Nevertheless, careful monitoring of these reactions gave no evidence of a *trihapto* intermediate. The indenyl system appears to behave in an identical manner to the cyclopentadienyl ligand in this respect.

In view of the above results, the reactions of phosphine and phosphite substituted manganese carbonyl halide complexes were investigated. By replacing carbonyl ligands with better donor/poorer acceptor ligands, the *trihapto* bonding mode might be favoured. It was also of interest to test the generality of the reaction and to see if this was another route to substituted complexes of the type $(\eta^5\text{-}1\text{-}C_9H_6X)$-$Mn(CO)_{3-n}L_n$ where n = 1 or 2.

Treatment of *cis*-$Mn(CO)_4PPh_3Br$ with diazoindene resulted in the isolation of $(\eta^5\text{-}1\text{-}C_9H_6Br)$-$Mn(CO)_3$. Thus the phosphine is lost instead of the CO from the probable *monohapto* or *trihapto* intermediates. This may be due to the greater *trans* effect of the CO [26] and the *cis*-labilizing ability of the halogen [10]. The other isomer *trans*-Mn-

*While this work was in progress other workers communicated the preparation of these complexes [21].

TABLE II. Products from $Mn(CO)_3L_2X + C_9H_6N_2$.

Starting Material	(η^5-1-C_9H_6X)-$Mn(CO)_3$[a]	(η^5-1-C_9H_6X)-$Mn(CO)_2[P(OPh)_3]$[a]	*mer*-$Mn(CO)_3$-$[P(OPh)_3]_2X$	*fac*-$Mn(CO)_3$-$[P(OPh)_3]_2X$
mer-$Mn(CO)_3[P(OPh)_3]_2Cl$	trace	trace	54%	7%
fac-$Mn(CO)_3[P(OPh)_3]_2Cl$	trace	trace	30%	–
mer-$Mn(CO)_3[P(OPh)_3]_2Br$	trace	trace	50%	10%
fac-$Mn(CO)_3[P(OPh)_3]_2Br$	trace	trace	25%	15%

[a]Trace amounts identified by infrared.

$(CO)_4PPh_3Br$ gave complete decomposition when treated in a similar fashion. The analogous phosphite complex, *cis*-$Mn(CO)_4P(OPh)_3Br$, upon reaction gave *mer*-$Mn(CO)_3[P(OPh)_3]_2Br$ as the main product which was identified by comparison to an authentic sample. Only a trace of the tricarbonyl insertion product, (η^5-1-C_9H_6Br)$Mn(CO)_3$ was detected by its infrared spectrum. Thus, complexes of the type (η^5-1-C_9H_6X)$Mn(CO)_2L$ were not accessible by this route.

Both the *fac* and the *mer* isomers of the complexes $Mn(CO)_3[P(OPh)_3]_2X$, where X = Cl and Br, reacted slowly with diazoindene at room temperature. Thus starting complex was always recovered along with traces of insertion products (Table II). The isolation of the *mer* isomer from *fac* starting complex, and *vice versa* to a lesser extent, indicates the tendency for these complexes to isomerize. When *fac*-$Mn(CO)_3[P(OPh)_3]_2Cl$ was dissolved in THF and stirred overnight it almost completely isomerized to the *mer* form. This did not occur in $CHCl_3$; unfortunately, there was no reaction with diazoindene in this solvent and the starting materials were recovered. Because of this it is not possible to determine if the *fac* compound isomerized before reacting. The other products include traces of (η^5-1-C_9H_6X)$Mn(CO)_3$ identified by its infrared spectrum and traces of another type of complex which was identified as the dicarbonyl phosphite complex (η^5-1-C_9H_6X)$Mn(CO)_2P(OPh)_3$. The characterization of the latter compound is based on its infrared spectrum in the carbonyl region (Table I). The complexity of these systems precludes discussion of the mechanisms involved.

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