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CYCLOMETALLATION REACTIONS

XII*. ON THE EFFECT OF VARIOUS LEAVING GROUPS ON INTERNAL METALLATION REACTIONS WITH ALKYLMANGANESE COMPLEXES

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Summary

The interaction of azobenzene and $MnR(CO)_5$ (R = Me, Et, CH_2Ph, $CH_2C_6Me_5$, $COCF_3$, $COCH_2C_6F_5$, $COCH_2OPh$, Ph or C_6F_5) affords $\overline{Mn(C_6H_4N{=}N}Ph)(CO)_4$, together with a binuclear complex $Mn_2(CO)_6(C_{12}H_{10}N_2)$ in some cases. The metallation reaction is shown to proceed most readily with $Mn(CH_2Ph)(CO)_5$; with this reagent, the metallated complexes $\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_3[PMe_2(CH_2Ph)]$ (two isomers) and $\overline{Mn(C_6H_4CH_2As}Me_2)(CO)_4$ have been obtained on treatment with $EMe_2(CH_2Ph)$ (E = P and As, respectively).

Introduction

Metallation of azobenzene by transition metal substrates to give complexes containing the chelating 2-(phenylazo)phenyl-*C,N'* ligand occurs with elimination of the *ortho*-hydrogen atom as a variety of small molecules, such as HCl, C_5H_6, etc. [2]. Our earliest studies revealed that methyl groups are particularly good leaving groups, being removed as methane [3]. Other examples include the intramolecular metallation of $RhMe(PPh_3)_3$ [4], the reaction between metallated phosphine complexes and $MMe(CO)_5$ (M = Mn, Re) to give a multitude of products, including I [5], the metallation of aryl ketones giving II [6], for example, and the synthesis of the metallocycle III by elimination of methane from IV [7].

Little is known of the factors involved in reactions of this type, and we report herein the results of a qualitative survey of the reactivity of various $MnR(CO)_5$ complexes towards metallation of azobenzene. During the course of this work, we found that $Mn(CH_2Ph)(CO)_5$ is more efficient at promoting these

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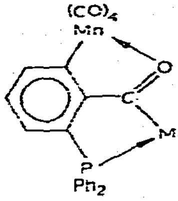
reactions than is the methyl compound, and we describe use of the benzyl complex to synthesise complexes containing internally metallated tertiary phosphine and arsine ligands, reactions which do not occur using $MnMe(CO)_5$.



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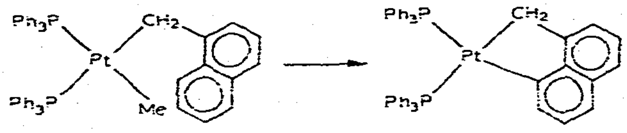

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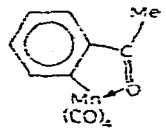

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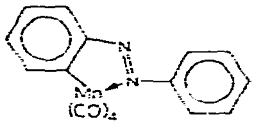

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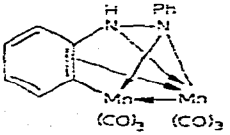

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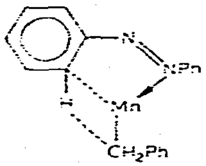

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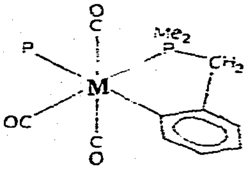

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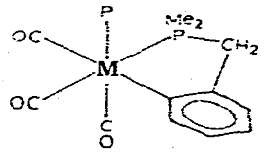

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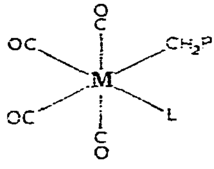
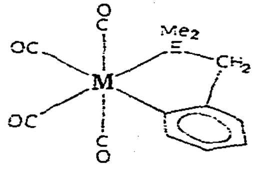


(IX) L = $PMe_2(CH_2Ph)$
(XI) L = PMe_2Ph



(X) E = P
(XII) E = As

P = $PMe_2(CH_2Ph)$: M = Mn

Several complexes containing *ortho*-metallated dimethylbenzylamine ligands have been reported. Thus Li_2PdCl_4 or Na_2PtCl_4 readily react with the parent tertiary amine to give $[\overline{M(C_6H_4CH_2NMe_2)}Cl]_2$ (M = Pd or Pt, respectively) [8], while $MnMe(CO)_5$ affords $\overline{Mn(C_6H_4CH_2N}Me_2)(CO)_4$ [9], which has been characterised by an X-ray diffraction study [10]. Use of the *ortho*-lithio derivative has given $\overline{Co(C_6H_4CH_2N}Me_2)_3$ [11], and similar reactions have been used to prepare $\overline{M(C_6H_4CH_2E}Me_2)_2$ (M = Ni, Pd or Pt; E = N [12] or As [13]). In contrast, we did not observe any metallation reactions in a wide range of complexes containing the ligands $PMe_2(CH_2Ph)$ or $AsMe_2(CH_2Ph)$ [14]. Indeed, little has been reported concerning cyclometallation reactions of arsenic donor ligands. Heating $IrCl(AsPh_3)_3$ in refluxing benzene for 6 h is reported to give good yields of $\overline{IrHCl(C_6H_4As}Ph_2)(AsPh_3)_2$ [15], and metallation of $AsMe_2(C_{10}H_7)$ ($C_{10}H_7$ =

1-naphthyl) in the *peri* position by platinum has been described [16]. The chromium complex $\overline{Cr(C_6H_4CH_2AsMe_2)_3}$ has been obtained from $CrCl_3$ and *o*-$LiC_6H_4CH_2AsMe_2$ [17].

Results and discussion

Metallation reactions using the complexes $MnR(CO)_5$

In an attempt to gain some insight into the role of the R group in cyclometallation reactions of $MnR(CO)_5$, the behaviour of selected alkyl- and arylmanganese carbonyls in reactions with azobenzene was examined. We did not attempt a detailed kinetic study, but comparative reactions were carried out under standard conditions. Typically, equimolar proportions of $MnR(CO)_5$ and azobenzene were heated together in refluxing methylcyclohexane (b.p. 100°C), while monitoring the $\nu(CO)$ region of the infrared spectrum. The times after which the $\nu(CO)$ bands of the initial $MnR(CO)_5$ complex were no longer apparent were noted. The products from these reactions, which were either the long-known compound [18] $\overline{Mn(C_6H_4N{=}N}Ph)(CO)_4$ (V) or the binuclear complex $Mn_2(CO)_6(C_{12}H_{10}N_2)$ formulated with structure VI [19], or occasionally both, were isolated by chromatography and sublimation, and identified by comparison with authentic samples.

In the earlier work [3] high yields of V and the rhenium analogue were obtained in relatively short times from reactions between azobenzene and $MMe(CO)_5$ (M = Mn or Re) at *ca* 120°C (Mn, 3h, 93%; Re, 6h, 80%). In the present series of experiments, carried out at somewhat lower temperatures, periodic examination of the infrared spectra of reaction mixtures indicated that no $MnMe(CO)_5$ remained after 4 h; under these conditions the isolated yield of V was around 40%.

For R = Et or benzyl, the same result was achieved after only 2 h and 1 h, respectively. The pentamethylbenzyl complex appeared to react very readily, but afforded only a low yield of V, together with substantial amounts of $Mn_2(CO)_{10}$. This result presumably reflects the tendency for thermal decomposition of $MnR(CO)_5$ into $Mn_2(CO)_{10}$ and R_2 [20], a process facilitated by the presence of the permethylated phenyl group. The binuclear complex was obtained in poor yield from reactions using complexes $MnR(CO)_5$ where R = Ph, C_6F_5 or $CH_2C_6F_5$, while the phenoxymethyl derivative afforded significant amounts of both azobenzene derivatives V and VI.

Decarbonylation was a common first step in the reactions of the acylmanganese complexes, as shown by a rapid reduction in intensity of the ν(acyl CO) band, with the simultaneous appearance of $\nu(CO)$ bands of the corresponding alkyl or aryl complexes. Cyclometallation occurred by reaction between azobenzene and the decarbonylated complexes; in no instance was any evidence obtained for the formation of complexes of the type $Mn(COR)(CO)_4(PhN{=}NPh)$ or $\overline{Mn(COC_6H_4N{=}N}Ph)(CO)_n$ (*n* = 4 or 5).

The only reaction observed using $Mn(CH_2CH{=}CH_2)(CO)_5$ was decarbonylation to form the η^3-allyl complex, which did not react further over a period of 24 h. This lack of reactivity contrasts with the ready formation of $\overline{Pt(C_6H_4N{=}N}Ph)(\eta\text{-}C_5H_5)$ in the reaction between azobenzene and $Pt(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)$ [21], with elimination of propene, probably as a result of the tendency for nickel, palladium and platinum η^3-allyls to react with donor ligands to form η^1-allylic intermediates [22].

We do not have enough information to distinguish between the steric, electronic and thermodynamic effects which undoubtedly influence this reaction. Our results are consistent with a mechanism involving an initial coordination of one of the azobenzene nitrogens to manganese, resulting in a build-up of electron density on the metal atom, which may be more or less dispersed in the R group, depending on the nature of R. The resulting intermediate then undergoes a concerted reaction involving cleavage of the Mn—C σ bond, and of the *ortho*-C—H bond, to give RH and complex V. A four-centre transition state such as VII may be written. It is conceivable that the initial coordination of the azo function results in migration of the R group to the aryl C—H region, akin to the transfer of methyl from manganese to CO found in the reaction between $MnMe(CO)_5$ and PPh_3, for example.

When we come to consider the differing effects of the various R groups, it is not clear which factor takes precedence. The clearest result, the more facile metallation observed for R = CH_2Ph over R = Me, is probably related to the greater thermodynamic stability of the resulting hydrocarbon (toluene vs. methane). The total lack of reaction with R = CF_3 may reflect a greater strength of the Mn—CF_3 over Mn—CH_3, although this has been questioned. The exact manner of formation of complex VI is not clear at present, although formally it results from the 1,3-addition of $HMn(CO)_5$ across the N=NMn system of V. In one case (R = CH_2OPh), this reaction becomes competitive with the formation of V, both products being found in approximately equimolar proportions.

Metallation of $PMe_2(CH_2Ph)$ and $AsMe_2(CH_2Ph)$

The most tangible result of the work described above is the demonstration that for manganese, at least, the readily-accessible benzyl metal complexes are much more efficient at promoting internal metallation reactions than are the corresponding methyl derivatives. We have further illustrated this result by preparing manganese complexes containing chelating $C_6H_4CH_2PMe_2$ and $C_6H_4CH_2AsMe_2$ ligands using $Mn(CH_2Ph)(CO)_5$ as a precursor.

A number of transition metal complexes containing benzyl dimethyl-phosphine and -arsine (L) have been described by us earlier [14], but we were not able to obtain any metallated complexes by pyrolysis of the derivatives $MnMe(CO)_3L_2$, halides such as MCl_2L_2 (M = Pd or Pt), or the carbonyls $Ru_3(CO)_9L_3$.

A reaction between equimolar amounts of $Mn(CH_2Ph)(CO)_5$ and $PMe_2(CH_2Ph)$, carried out 170°C in a sealed tube afforded only the binuclear complex $[Mn(CO)_4PMe_2(CH_2Ph)]_2$, characterised by the usual methods. It is of interest that a minor product obtained from the reaction between $MnMe(CO)_5$ and $PMe_2(CH_2Ph)$ is the tetrakis phosphine complex $[Mn(CO)_3\{PMe_2(CH_2Ph)\}_2]_2$.

The direct reaction between $Mn(CH_2Ph)(CO)_5$ and $PMe_2(CH_2Ph)$ in refluxing decalin gave a poor yield of a white solid, thought to be a mixture from its complex infrared $\nu(CO)$ spectrum. Repeated crystallisation effected separation into two isomers (VIIIa and b), for which analytical and mass spectral data were consistent with the formulation $\overline{Mn(C_6H_4CH_2PMe_2})(CO)_3[PMe_2(CH_2Ph)]$. The infrared spectrum of VIIIa showed three $\nu(CO)$ bands, characteristic of a *mer*-$M(CO)_3$ group, while the proton NMR spectrum (see below) confirmed the presence of the *ortho*-metallated aryl group, and showed the two PMe_2 groups were mutually *cis*. The second isomer VIIIb showed only two ν(CO) bands, characteristic of a *fac*-$M(CO)_3$ group, and the proton NMR spectrum again indicated mutually *cis*-PMe_2 groups. The illustrated structures satisfy all the spectroscopic data.

There is good evidence suggesting that the formation of these complexes proceeds via the monosubstituted derivative $Mn(CH_2Ph)(CO)_4[PMe_2(CH_2Ph)]$ (IX). This complex can be detected spectroscopically (IR) during the reaction, and can be isolated from a reaction stopped short of completion. Further, pyrolysis of an authentic sample of IX affords good yields of both VIIIa and VIIIb.

At lower temperatures, for example in refluxing toluene, the reaction between $Mn(CH_2Ph)(CO)_5$ and $PMe_2(CH_2Ph)$ affords $\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_4$ (X) as a white solid. The infrared spectrum contains the four ν(CO) bands expected for a *cis*-LL′M(CO)$_4$ complex, and the mass spectrum contained the ions $[P - n\ CO]^+$ (n = 0-4). The proton NMR spectrum was consistent with the presence of the *ortho*-metallated ligand.

Under the same conditions, a reaction using PMe_2Ph gave only the complex $Mn(CH_2Ph)(CO)_4(PMe_2Ph)$ (XI), characterised by the usual methods. On heating in 2-methoxyethanol in an attempt to induce metallation, slow decomposition to dark-coloured insoluble material occurred.

Cyclometallation of $AsMe_2(CH_2Ph)$ occurred on heating with $Mn(CH_2Ph)(CO)_5$ in refluxing decalin for 15 min. The yellow crystalline complex so obtained was characterised as $\overline{Mn(C_6H_4CH_2As}Me_2)(CO)_4$ (XII), the infrared spectrum containing four ν(CO) bands with relative intensities similar to those found for X. The proton NMR spectrum indicated the presence of the chelate metallated arsine ligand.

Attempts to induce an intermolecular metallation reaction, by simply heating $Mn(CH_2Ph)(CO)_5$ in refluxing decalin, resulted only in the rapid production of a yellow solution, shown to contain $Mn_2(CO)_{10}$ and 1,2-diphenylethane. The same result has been reported independently [20].

Proton NMR spectra

The major features of the proton NMR spectra of the complexes described above are collected in Table 1.

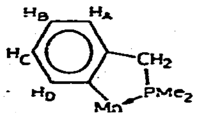
(a) $\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_4$ *(X).* Signals in the aromatic region result from the *ortho*-metallated ring, and are easily assigned [3]. The two lower field signals (from H_A and H_B) are four-line resonances as a result of coupling to their respective *ortho* and *meta* protons. Both CH_2 and Me resonances exhibit coupling to phosphorus.

(b) $\overline{Mn(C_6H_4CH_2As}Me_2)(CO)_4$ *(XII).* The spectrum of the arsine complex is similar to that of X, but with the aromatic resonances now well separated and resolved. In particular, the high-field signal (for H_C and H_D) is an AB quartet centred on τ 3.19, also showing coupling to the other ring protons. The CH_2 and Me resonances are both sharp singlets, at somewhat lower field than those found for X.

(c) $\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_3[PMe_2(CH_2Ph)]$ *(VIIIa and b).* In the spectra of these complexes, the H_B signal is completely obscured by the broad resonance of the aromatic protons of the non-chelating phosphine.

TABLE 1

PROTON NMR DATA FOR SOME MANGANESE COMPLEXES. CHEMICAL SHIFTS IN τ(ppm) AND COUPLING CONSTANTS IN Hz

		VIIIa[a]	VIIIb[a]	IX[b]	X[b]	XII[c]	$[\mathrm{Mn(CO)_4L}]_2$[b,d]
$\mathrm{Mn}\mathit{CH}_2\mathrm{Ph}$				7.85d			
$J(\mathrm{PCH_2})$				7.0			
$\mathrm{MnCH_2}\mathit{Ph}$				2.76m			
$\mathrm{P}\mathit{Me}_2\mathrm{CH_2Ph}$		8.85d, 9.08d	8.84d	8.60d			8.63d
$J(\mathrm{PMe})$		8.25, 8.0	7.25	8.3			7.6
$\mathrm{PMe_2}\mathit{CH}_2\mathrm{Ph}$		7.22m	6.80d	6.70d			6.73d
$J(\mathrm{PCH_2})$			5.5	6.6			6.0
$\mathrm{PMe_2CH_2}\mathit{Ph}$		ca. 2.95m	ca. 2.95m	2.76m			2.70m
$\overline{\mathrm{MnC_6H_4CH_2P}}\mathit{Me}_2$		9.36dd	8.86d		9.38d	8.44s	
$J(\mathrm{PMe})$		7.0, 7.25	9.0		9.0		
$\overline{\mathrm{MnC_6H_4}\mathit{CH}_2\mathrm{P}}\mathrm{Me_2}$		7.32d	6.98d		7.63d	7.59s	
$J(\mathrm{PCH_2})$		5.0	9.5		10.0		
	H_A	1.90dd	2.36dd		2.38dd	2.49dd	
	H_D	ca. 2.95m	ca. 2.95m		2.86dd	2.92dd	
	H_{B+C}	3.49m	3.27m		3.03m	3.19m	
	J_{AB}	5.4	5.5		8.0	5.5	
	J_{AC}	3.0	2.1		3.5	3.5	
	J_{BD}				10.0	5.25	

[a] C_6D_6. [b] $CDCl_3$. [c] CS_2. [d] L = $PMe_2(CH_2Ph)$.

For VIIIa, the H_A signal appears at τ 1.90 as a quartet, as found for X. The presence of two non-equivalent phosphine ligands is shown by the appearance of two CH_2 resonances, and four Me resonances; the latter feature results from the gross asymmetry of the complex, whereby the two methyl groups on each phosphorus are in different environments. Comparison with X suggests assignment of the signals at τ 7.32 (CH_2) and 9.36 (Me) to the metallated phosphine ligand. In the spectrum of VIIIb, H_A is at considerably higher field, at τ 2.36, while the Me protons appear as two resonances.

(d) $Mn(CH_2Ph)(CO)_2[PMe_2(CH_2Ph)]$ (XI). The four resonances in the spectrum of XI can be readily assigned, the two types of methylene group being well-separated at τ 6.70 (PCH_2) and 7.85 ($PhCH_2$).

Experimental

Spectra were recorded on Perkin—Elmer 257 (infrared), Varian Associates HA 100 [^{1}H (100 MHz) or ^{19}F (94.07 MHz) NMR], or AEI-GEC MS 902 (mass) instruments. Analytical and ν(CO) data are presented in Table 2.

Reactions were normally carried out under nitrogen, although the pure complexes were generally air-stable, and no special precautions were taken to exclude oxygen during work up procedures. Chromatography was on columns of Florisil, initially packed in light petroleum. Solvents were dried and distilled before use. Light petroleum refers to a fraction b.p. 40-60°C. Benzyldimethylphosphine and -arsine were prepared as described previously [14].

TABLE 2

ANALYTICAL DATA AND INFRARED SPECTRA OF SOME NEW MANGANESE COMPLEXES

Complex		M.P. (°C)	Found (calcd.) (%) C	H	P	M^{+a}	ν(CO) (cyclohexane) (cm^{-1})
$Mn(CH_2C_6Me_5)(CO)_5$		130-131	57,3 (57,4)	4,95 (4,8)		356 (356)	2106m, 2042w, 2012s, 1990s
$Mn(COCH_2C_6F_5)(CO)_5$		99-100	38,8 (38,7)	0,6 (0,45)		376^b (404)	2122w, 2061w, 2020s, 2011s, 2003m, 1631s (acyl CO)
$Mn(COCH_2OPh)(CO)_5$		91-92	47,6 (47,3)	2,4 (2,2)		302^b (330)	2118m, 2054w, 2024s, 2004s, 1642s (acyl CO)
$[Mn(CO)_4PMe_2(CH_2Ph)]_2$		151-152	48,7 (48,9)	4,15 (4,05)			2054w, 1983m, 1965(sh), 1955vs, 1925(sh), 1921m
$Mn(CH_2Ph)(CO)_4[PMe_2(CH_2Ph)]$	(IX)	64-65	58,4 (58,6)	4,0 (4,9)		410 (410)	2056m, 1991m, 1964s, 1940m
$\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_4$	(X)	53-54	49,3 (49,2)	3,95 (3,8)	9,65 (9,75)	318 (318)	2065m, 1989m, 1975s, 1950s
$\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_3[PMe_2(CH_2Ph)]$	(VIIIa)	82-83	57,05 (57,0)	5,7 (5,65)	14,0 (14,0)	442 (442)	2003vs, 1931s, 1905s
$\overline{Mn(C_6H_4CH_2P}Me_2)(CO)_3[PMe_2(CH_2Ph)]$	(VIIIb)	128-129	57,05 (57,0)	5,6 (5,65)	13,85 (14,0)	442 (442)	2033s, 1900m
$\overline{Mn(C_6H_4CH_2As}Me_2)(CO)_4$	(XII)	70-71	43,3 (43,4)	3,35 (3,3)		362 (362)	2067m, 1989m, 1978s, 1953s

[a] Mass spectrometry. [b] $[P - CO]^+$ (see text).

Syntheses of complexes $MnR(CO)_5$

The methyl, ethyl, phenyl, pentafluorophenyl, benzyl and trifluoroacetyl complexes $MnR(CO)_5$ were prepared by published methods.

The pentamethylbenzyl ($R = CH_2C_6Me_5$), pentafluorophenylacetyl ($R = COCH_2C_6F_5$) and the phenoxyacetyl ($R = COCH_2OPh$) derivatives were obtained by treating a tetrahydrofuran solution of sodium pentacarbonylmanganate with an equivalent amount of the appropriate halide ($C_6Me_5CH_2Br$, $C_6F_5CH_2COCl$ or $PhOCH_2COCl$, respectively) at room temperature for two hours. The reaction mixture was then filtered, solvent removed on a rotary evaporator, and the residue recrystallised from benzene—light petroleum mixtures to afford the pure product. So prepared were:

$Mn(CH_2C_6Me_5)(CO)_5$, pale yellow crystals, 55% yield; ^1H NMR (C_6D_6): τ 7.48s (br) (CH_2), 7.76s (br), 7.90s (br) (Me).

$Mn(COCH_2C_6F_5)(CO)_5$, white crystals, 41% yield; ^1H NMR (C_6D_6): τ 6.28s (br); ^{19}F NMR (C_6D_6): $F_{2,6}$ 145.8, $F_{3,5}$ 167.1, F_4 160.0 ppm.

$Mn(COCH_2OPh)(CO)_5$, white crystals, 56% yield; ^1H NMR (C_6D_6): τ 2.84m, 3.26m (C_6H_5), 6.29s (CH_2).

In common with many other acyl complexes, the mass spectra of $Mn(COR)(CO)_5$ ($R = CH_2C_6F_5$ and CH_2OPh) did not contain parent ions, decarbonylation occurring to give the parent ion of the corresponding alkyl complex, i.e. $[P - CO]^+$. However, the presence of a strong ion at *m/e* 233 ($[Mn(CO)_6]^+$) together with the ν(acyl CO) band in the infrared spectrum between 1630-1645 cm^{-1}, confirmed the identity of these acyl derivatives.

Reactions between $MnR(CO)_5$ and azobenzene

A mixture of equimolar amounts of the alkyl or aryl complexes and azobenzene was refluxed in methylcyclohexane (b.p. 100°C), the reaction being monitored by periodic examination of the ν(CO) region of the infrared spectrum. The reaction was considered to be complete when the ν(CO) bands of the initial $MnR(CO)_5$ complex were no longer present. Solvent was then removed (rotary evaporator), and the residue was chromatographed to give three possible fractions: azobenzene (eluted with light petroleum), $\overline{Mn(C_6H_4N=N}Ph)(CO)_4$ (V) (eluted with 1/99 ether/light petroleum) or $Mn_2(CO)_6(C_{12}H_{10}N_2)$ (VI) (eluted with 1/9 ether/light petroleum). Purification of the compounds was achieved by sublimation [azobenzene, 35°C/0.01 Torr; $Mn(azb)(CO)_4$, 90°C/0.01 Torr] or recrystallisation from hexane, and the products were characterised by comparison with authentic samples.

The individual experimental details are summarised in Table 3.

Reactions between $Mn(CH_2Ph)(CO)_5$ and PMe_2CH_2Ph

(a) A mixture of $Mn(CH_2Ph)(CO)_5$ (400 mg, 1.4 mmol) and $PMe_2(CH_2Ph)$ (213 mg, 1.4 mmol) in cyclohexane (70 ml) was irradiated for 72 h at room temperature. Filtration, removal of solvent (rotary evaporator), and recrystallisation of the residue (hexane) gave yellow $Mn(CH_2Ph)(CO)_4(PMe_2CH_2Ph)$ (XI) (344 mg, 60%).

(b) The benzyl complex (100 mg, 0.35 mmol) and the phosphine (53 mg, 0.35 mmol) were heated together for 4 h in refluxing toluene (40 ml). Chromatography of the concentrated reaction mixture gave the product, eluted with 1/9 ether/

TABLE 3

REACTIONS BETWEEN $MnR(CO)_5$ AND AZOBENZENE

R (mg/mmol)	Azobenzene (mg/mmol)	Solvent (ml)	Product	% Conversion[a]	Reaction time (h)
Me 100/0.48	87/0.48	72	$Mn(azb)(CO)_4$[b]	40	4.0
Et 90/0.40	73/0.40	60	$Mn(azb)(CO)_4$	56	2.0
CH_2Ph 100/0.35	64/0.35	53	$Mn(azb)(CO)_4$	43	1.0
$CH_2C_6Me_5$ 95/0.27	50/0.27	41	$Mn(azb)(CO)_4$	14	1.0
			$Mn_2(CO)_{10}$	37[c]	
Ph 100/0.37	67/0.37	56	$Mn_2(CO)_6(C_{12}H_{10}N_2)$	14	2.0
C_6F_5 100/0.28	51/0.28	42	$Mn_2(CO)_6(C_{12}H_{10}N_2)$	17	3.5
$COCH_2C_6F_5$ 100/0.25	45/0.25	38	$Mn_2(CO)_6(C_{12}H_{10}N_2)$	39	2.3
$COCH_2OPh$ 40/0.28	51/0.28	42	$Mn(azb)(CO)_4$	7	2.2
			$Mn_2(CO)_6(C_{12}H_{10}N_2)$	34	

[a] Based on reacted azobenzene. [b] azb = 2-(phenylazo)phenyl-*C,N'*. [c] Based on $Mn(CH_2C_6Me_5)(CO)_5$.

hexane, which was recrystallised from hexane to give white $Mn(C_6H_4CH_2PMe_2)(CO)_4$ (X) (68 mg, 61%).

(c) Heating a mixture of the benzyl complex (286 mg, 1.0 mmol) and $PMe_2(CH_2Ph)$ (152 mg, 1.0 mmol) in refluxing decalin (8 ml) for 2 h. After cooling to —10°C, the resulting solution was filtered, evaporated, and the residue fractionally recrystallised from hexane to give two isomers of $Mn(C_6H_4CH_2PMe_2)(CO)_3[PMe_2(CH_2Ph)]$. Both were white, the least soluble being VIIIa (53 mg, 12%), while VIIIb (70 mg, 16%) was recovered from the mother liquors.

Reaction between $Mn(CH_2Ph)(CO)_5$ and $AsMe_2CH_2Ph$

A mixture of $Mn(CH_2Ph)(CO)_5$ (400 mg, 1.4 mmol) and the arsine (275 mg, 1.4 mmol) was heated for 15 min in refluxing decalin (4 ml). Subsequent chromatography afforded a yellow band, eluted with 1/19 ether/hexane, which was evaporated and recrystallised (hexane) to give yellow $Mn(C_6H_4CH_2AsMe_2)(CO)_4$ (XII) (127 mg, 25%).

Reaction between $Mn(CH_2Ph)(CO)_5$ and dimethylphenylphosphine

A mixture of the phosphine (48 mg, 0.35 mmol) and $Mn(CH_2Ph)(CO)_5$ (100 mg, 0.35 mmol) was heated in refluxing petroleum ether (30 ml) for 1 h. Chromatography gave a yellow band (1/4 ether—hexane) which afforded $Mn(CH_2Ph)(CO)_4(PMe_2Ph)$ as a yellow oil identified spectroscopically [*M* (mass spectrometry): 396; $C_{19}H_{18}MnO_4P$ calcd.: 396). Infrared (cyclohexane): $\nu(CO)$ at 2059m, 1992m, 1967s, 1940m cm^{-1}.

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