275. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. IV[1]). Preparation and Properties of Some Rhodium and Iridium Complexes of 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene

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Summary

The bidentate phosphine 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) has been used to prepare the mononuclear, square planar complexes *trans*-[MX(CO)(**1**)] and *trans*-[M(CO)(CH_3CN)(**1**)][BF_4] (M = Rh, Ir; X = Cl, Br, I, NCS). It is found that the tendency of these complexes to form adducts with CO, O_2 and SO_2 is significantly lower than that of the corresponding Ph_3P complexes. The oxidative-addition reactions of complexes *trans*-[IrX(CO)(**1**)] with hydrogen halides give the six-coordinate species [$IrHX_2$(CO)(**1**)]. The complexes [IrH_2I(CO)(**1**)] and [IrH_2L(CO)(**1**)][BF_4] (L = CO and CH_3CN) have been obtained from hydrogen and the corresponding substrates. The model compounds *trans*-[MCl(CO)$(Ph_2PCH_2Ph)_2$] (M = Rh, Ir), *trans*-[Ir(CO)(CH_3CN)$(Ph_2PCH_2Ph)_2$][BF_4], [$IrHCl_2$(CO)$(Ph_2PCH_2Ph)_2$] and [$IrH_2(CO)_2(Ph_2PCH_2Ph)_2$][$BF_4$] have been prepared and their special parameters are compared with those of the corresponding complexes of ligand **1**. The influence of the static requirements of this ligand on the chemistry of its rhodium and iridium complexes is discussed.

1. Introduction. - The chemistry of complexes of the type *trans*-[MX(CO)$(R_3P)_2$] (M = Rh, Ir; X = halide; R = alkyl or aryl) has been extensively studied [2]. Complexes of this type have received particular attention as their reactions with small neutral molecules are believed to be related to some of the steps in the mechanisms postulated in organometallic synthetic processes: *e.g.* hydroformylation, homogeneous hydrogenation and olefin oligomerization which are catalysed by related, coordinatively unsaturated complexes of d^8- and d^{10}-metal centres [3]. As some of the mechanistic aspects of the oxidative addition and related reactions are still the subject of debate, their study using complexes containing fairly rigid bidentate ligands such as **1** appeared worth-while.

The synthesis of the bidentate ligand 2,11-bis(diphenylphosphinomethyl)-benzo[*c*]phenanthrene (**1**) has been reported in an earlier publication [4] and its crystal structure determined [5].

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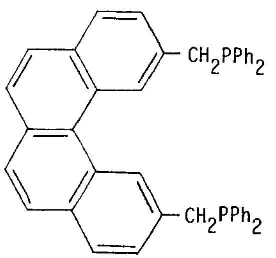
[1]) Part III: see [1].



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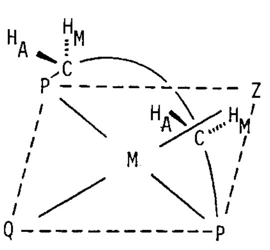

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As discussed in Part I of this series [4], ligand **1** is best suited for the formation of square planar complexes of type **2** and some of these (M = Ni, Pd, Pt; Q = Z = halide) have been described in an earlier publication [6].

It was also pointed out [4] that examination of molecular models indicates that the formation of five- and six-coordinate species containing ligand **1** is likely to require distortions of the regular coordination polyhedra and/or of the organic backbone.

As the oxidative-addition reactions of coordinatively unsaturated complexes of rhodium(I) and iridium(I) generally result in the formation of five- and six-coordinate species, it was of interest to study the effect of the steric requirements of ligand **1** on the reactivity of its rhodium(I) and iridium(I) complexes. This paper reports such a study. The preparation of related complexes with two molecules of the ligand Ph_2PCH_2Ph, which contains a phosphorus atom with electron-donating properties similar to those of the phosphorus atoms in ligand **1**, is also described.

2. Results and Discussion. - 2.1. *Square planar complexes.* The complex *trans*-[RhCl(CO)(**1**)] was prepared by reaction of **1** with $[Rh_2Cl_2(CO)_4]$ [7]. Treatment of *trans*-[RhCl(CO)(**1**)] with $Ag[BF_4]$ in CH_3CN gave *trans*-[Rh(CO)(CH_3CN)(**1**)] $[BF_4]$ and acetone solutions of this salt reacted with ethanolic solutions of NaBr, NaI or NH_4NCS to give the corresponding *trans*-[RhX(CO)(**1**)] species.

The complex *trans*-[IrCl(CO)(**1**)] could be obtained by several methods: (a) by refluxing for 6 h a solution of $IrCl_3 \cdot nH_2O$ in 2-methoxyethanol/water 9:1 in a stream of CO and then adding ligand **1**; (b) by reaction of **1** with $[IrCl(CO)_2$(*p*-toluidine)] [8]; or (c) by reaction of **1** with $[AsPh_4][IrCl_2(CO)_2]$ [9]. The complexes *trans*-[Ir(CO)(CH_3CN)(**1**)]$[BF_4]$ and *trans*-[IrX(CO)(**1**)] (X = Br, I, NCS) were obtained as described for the corresponding rhodium compounds.

The complexes *trans*-[MX(CO)(**1**)] are slightly soluble in chlorinated hydrocarbon solvents and insoluble in most other organic solvents. The salts *trans*-[M(CO)(CH_3CN)(**1**)]$[BF_4]$ are soluble in chlorinated hydrocarbon solvents, acetone, THF and CH_3CN but sparingly soluble in benzene or ethanol. They slowly react with $CHCl_3$ to give *trans*-[MCl(CO)(**1**)].

In order to compare the spectral data of complexes containing ligand **1** with those of analogous complexes of a monodentate ligand having similar electronic properties, the complexes *trans*-$[MCl(CO)(Ph_2PCH_2Ph)_2]$ (M = Rh, Ir) and *trans*-$[Ir(CO)(CH_3CN)(Ph_2PCH_2Ph)_2][BF_4]$ were also prepared. These diphenylbenzylphosphine derivatives are fully analogous to those with other phosphines reported in the literature [2].

Some physical data for the complexes prepared are given in *Table 1* and their analytical data in *Table 2*. The salient NMR. data are listed in *Table 3*.

The ^{1}H-NMR. data for complexes *trans*-[MX(CO)(**1**)] and *trans*-[M(CO)(CH_3CN)(**1**)][BF_4] are similar to those observed for complexes *trans*-[MX_2(**1**)] (M = Ni, Pd, Pt; X = Cl, Br, I) [6] with the notable exception that resonances due to the $-CH_2-$ protons generally give a set of four triplets which can be assigned to the spin system *AMXX'M'A'*. As this pattern is observed only when the ligands Q and Z in complexes of type **2** are different, it can be presumed that the orientations of H_A and H_M in structure **2** are restricted in such a way that they experience different average shielding effects from the Q and Z ligands. In this context it is worth noting that the ^{1}H-NMR. shifts of Me_3P complexes of the platinum metals are more strongly dependent on the shielding effects of the *cis*-ligands than on metal charge or *trans*-influence considerations [10]. Double resonance experiments on *trans*-[Ir(NCS)(CO)(**1**)] (**11**) have established that the two hydrogen atoms of the $-CH_2-$ group are coupled and that the value of their coupling constant, (see J_1 on *Table 3*) is of the normal order of magnitude for geminal methylene protons [11].

The ^{1}H-NMR. resonances of the $-CH_2-$ group in *trans*-[Ir(CO)(CH_3CN)(**1**)][BF_4] (**12**) in $CDCl_3$ appear as a complex multiplet, approximately defined by the spin system *ABXX'B'A'*, which arises from the small difference in chemical shift between H_A and H_B. It can be presumed that differences in shielding effects

Table 1. *Some Physical Data and Yields for Rhodium and Iridium Complexes with Ligand* **1** *and* Ph_2PCH_2Ph

	Compound	Colour	Dec. p.[a])	Yield (%)	$\tilde{\nu}_{CO}$[b]) [cm^{-1}]	$\tilde{\nu}_{CN}$ or $\tilde{\nu}_{IrH}$ [cm^{-1}]
3	*trans*-[RhCl(CO)(**1**)]	pale yellow	230°	80	1980	
4	*trans*-[RhBr(CO)(**1**)]	yellow	280°	85	1980	
5	*trans*-[RhI(CO)(**1**)]	orange	260°	95	1980	
6	*trans*-[Rh(NCS)(CO)(**1**)]	lemon yellow	280°	80	1990	2090
7	*trans*-[Rh(CO)(CH_3CN)(**1**)][BF_4]	yellow	170°	75	2010	
8	*trans*-[IrCl(CO)(**1**)]	yellow	280°	80-90	1965	
9	*trans*-[IrBr(CO)(**1**)]	yellow	280°	63	1965	
10	*trans*-[IrI(CO)(**1**)]	orange	270°	75	1970	
11	*trans*-[Ir(NCS)(CO)(**1**)]	greenish yellow	280°	48	1980	2090
12	*trans*-[Ir(CO)(CH_3CN)(**1**)][BF_4]	yellow	180°	27	2000	
13	*trans*-[RhCl(CO)(Ph_2PCH_2Ph)$_2$]	yellow	150°	92	1970	
14	*trans*-[IrCl(CO)(Ph_2PCH_2Ph)$_2$]	yellow	150°	57	1965	
15	*trans*-[Ir(CO)(CH_3CN)(Ph_2PCH_2Ph)$_2$][BF_4]	yellow	190°	79	2000	
16	[$IrHCl_2$(CO)(**1**)]	v. pale yellow	280°	44	2025	2175
17	[$IrHBr_2$(CO)(**1**)]	v. pale yellow	280°	60	2035	2180
18	[$IrHI_2$(CO)(**1**)]	yellow	260°	38	2030	2160
19	[$IrHCl_2$(CO)(Ph_2PCH_2Ph)$_2$]	colourless	220°	41	2050	2120
20	[IrH_2I(CO)(**1**)]	v. pale yellow	250°	80	2000	2120, 2175[c])
21	[IrH_2(CO)(CH_3CN)(**1**)][BF_4]	colourless	205°	50	2010	2120, 2200[d])
22	[IrH_2(CO)$_2$(**1**)][BF_4]	colourless	260°	35	2045	2080, 2155
23	[IrH_2(CO)$_2$(Ph_2PCH_2Ph)$_2$][BF_4]	colourless	220°	25	2040	2075, 2145

[a]) Gradual decomposition occurs above the temperature stated. [b]) Recorded in $CHCl_3$ solution. [c]) Recorded in a nujol mull; shoulders at 2190 and 2100 are also observed. [d]) Recorded in a nujol mull.

Table 2. *Analytical and Molecular Weight Data for Rhodium and Iridium Complexes of Ligand* **1** *and* Ph_2PCH_2Ph

Compd.	C %		H %		P %		X %[a])		Mol.wt[b])	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
3	68.36	68.32	4.40	4.33	7.80	7.82	4.54	4.48	797	791.02
4	64.57	64.69	4.16	4.10	7.34	7.42	9.69	9.56	838	835.48
5	61.11	61.24	3.95	3.88	7.15	7.03	14.48	14.40	889	882.47
6	67.68	67.90	4.56	4.21	7.29	7.50	1.58	1.72	848	813.65
7	64.18	63.89	4.16	4.20			1.46	1.59	832	883.43
8	61.43	61.33	3.98	3.89	7.08	7.04	3.86	4.03	874	879.31
9	58.45	58.38	3.79	3.70	6.78	6.69	8.51	8.63	942	924.77
10	55.70	55.56	3.70	3.52	6.20	6.37	12.99	13.03	968	971.76
11	61.28	61.13	3.85	3.77	6.68	6.87	1.58	1.55	928	902.94
12	58.09	58.03	4.05	3.83	5.24	6.02	1.38	1.44	950	972.72
13	65.14	65.15	4.85	4.77	8.51	8.62	4.98	4.93		718.96
14	57.88	57.95	4.32	4.24	7.48	7.66	4.28	4.39		808.25
15	54.57	54.67	4.18	4.14	6.79	6.88	1.50	1.56		900.67
16	58.67	58.95	3.84	3.85	6.60	6.76	7.85	7.73	917	915.77
17	53.56	53.74	3.56	3.51	6.07	6.16	15.97	15.39		1005.69
18	49.23	49.15	3.33	3.21	5.32	5.23	21.50	21.41	1071	1099.07
19	55.30	55.38	4.19	4.14	7.22	7.34	8.50	8.40		844.71
20	55.64	55.44	3.69	3.70					999	973.78
21	57.38	57.91	4.24	4.00	5.95	6.36	1.43	1.44		974.74
22	57.98	57.44	4.24	3.75	6.07	6.44			912	951.70
23	54.05	54.12	3.91	3.86	6.23	6.98				972.83

[a]) Halogen or nitrogen. [b]) These were determined osmometrically in CH_2Cl_2.

between CO and CH_3CN are smaller than those between CO and anionic ligands. This complex multiplet resolves into the 'normal' four sets of triplets when the spectrum of the same compound is measured in a mixture of $CDCl_3$ and C_6D_6. This solvent-dependence of the chemical shift of the $-CH_2$-protons is also observed for *trans*-[IrCl(CO)(**1**)] (**8**) (see *Table 3*). A more detailed discussion of the $-CH_2-$ ^{1}H-NMR. resonances in these and other complexes will be published at a later date [12].

It has not proved possible to reliably assign the ^{1}H-NMR. resonances of the coordinated CH_3CN in complexes **7**, **12** and **15** due to overlap with the solvent resonances.

As observed for complexes [MX_2(**1**)][6], the ^{1}H-NMR. resonances of the 1,12-ring protons of the benzo[*c*]phenanthrene moiety shift to lower fields on complex formation and their position is useful for diagnostic purposes.

^{13}C-NMR. spectra could be recorded only for the more soluble complexes, *i.e.* *trans*-[Rh(NCS)(CO)(**1**)] (**6**) and *trans*-[Ir(CO)(CH_3CN)(**1**)][BF_4] (**12**). In both cases the resonances of the $-CH_2$-groups appear as a 'virtually coupled' triplet defining an *ABX* spin system (see *Table 3*). The appearance of only one triplet supports the hypothesis that although the methylene *protons* are inequivalent both methylene *carbon atoms* of the organic ligand are equivalent.

^{31}P-NMR. spectra were obtained for all the complexes and are given in *Table 3*. The values of the chemical shifts and of the $|{}^1J({}^{103}Rh, {}^{31}P)|$ coupling constants fall

Table 3. *NMR. Parameters for Rhodium and Iridium Complexes of ligand* **1** *and of* Ph_2PCH_2Ph

Compound	$\delta_{1,12}$[a] [ppm]	δ_{-CH_2-}[b] [ppm]	δ_{-CH_2-}[c] [ppm]	J_1[d] [Hz]	J_2[e] [Hz]	$\delta^{31}P$[f] [ppm]	J_3[g] [Hz]	δIr-*H* [ppm]	J_4[h] [Hz]
3	10.47	5.28	3.64	14	9	28.16	124		
4	10.42	5.39	3.80	13.8	[i]	25.98	123		
5	10.36	5.58	4.08	14	8	22.86	122		
6[j]	10.30	4.68	3.75	13.5	9	28.01	125		
7[m]	10.17	[k]	[k]	[l]	[l]	27.98[m]	120		
7[n]	9.40	3.67	3.19	13	6				
8	10.50	5.23	3.82	13.8	9.5	21.72			
8[o]	10.56	5.07	3.10	14	9	22.07			
9	10.48	5.35	3.98	13.8	9.5	18.98			
10	10.44	5.56	3.98	14	9	14.51			
11	10.28	4.66	3.94	13.6	9.1	21.23			
12[p]	9.70	[q]	[q]	[i]	[i]	22.08			
13		4.04[r]			8.2	29.48	118		
14		4.14[r]			8.7	23.08			
15		4.08[r]			8.2	21.75			
16	9.91	5.42	3.72	13.2	9	6.47[s]		− 14.00	12
17	9.29	4.71	3.64	14.2	[t]	− 5.37[s]		− 14.17	12
18	9.15	4.60	4.05	14.5	8	− 21.07[s]		− 13.48	12
19		4.56[r]			10	− 0.76[s]		− 16.20	11
20	9.87	5.28	4.18	12	8.5	0.10[u]		[v]	[v]
21	9.50	4.50	4.20	13	6	4.46[u]		[x]	[x]
22	9.42	4.44[y]		8.8		− 3.22		− 9.57	14.6
23		3.98[y]		8.5		2.05		− 10.57	14.6
24[z]		3.98[y]		8.1		8.65		[z]	[z]
25[α]	9.83	4.88	3.32	13.8	9.4	18.46			
26[β]	9.36	4.46[y]			5	− 5.3			
27[γ]	9.30	3.56[δ]			7.5	26.19[h]	116		
28[ε]	8.82	4.50	3.66	14.5	8.5-9.5	10.36			

[a] Shift of protons at positions 1 and 12 on the benzo[*c*]phenanthrene ring. [b] δ for H_A (defined arbitrarily). [c] δ for H_M(defined arbitrarily). [d] $|^2J(H_A,H_M)|$. [e] $|^2J(^{31}P,^1H)+^4J(^{31}P,^1H)|$ for $-CH_2-$. These are average values of coupling constants to protons H_A and H_M. [f] Relative to H_3PO_4 with a positive value indicating a shift to lower field. [g] $|J(^{103}Rh, ^{31}P)|$. [h] $|^2J(^{31}P,^1H_{hydridic})|$. [i] Not resolved. [j] For $-CH_2-$, $\delta^{13}C = 36.7$ ppm and $|^1J(^{31}P,^{13}C)+^3J(^{31}P,^{13}C)| = 25$ Hz. [k] Complex multiplet centred around 4.42 ppm most likely to be described by the spin system *ABXX'B'A'*. [l] No reliable values of these parameters could be calculated from the spectra obtained. [m] Measured in d_6-acetone. [n] Measured in $CDCl_3/C_6D_6$ 1:1. [o] Measured in C_6D_6. [p] For $-CH_2-$, $\delta^{13}C = 37.0$ ppm and $|^1J(^{31}P,^{13}C)+^3J(^{31}P,^{13}C)| = 30.9$ Hz. [q] Complex multiplet centred around 4.62 ppm. [r] δ_{-CH_2-} for the spin system $A_2XX'A'_2$. [s] When the spectrum was recorded under 'off-resonance' conditions a doublet with separation of 7-9 Hz was observed. [t] $J_2 = 10$ Hz and 8 Hz for the *A* and *B* parts of the spin system. [u] When the spectrum was recorded under 'off-resonance' conditions this resonance appeared as a triplet. [v] The hydrido-ions are not equivalent: δIr-H = − 9.08 and δIr-H' = − 16.12 ppm, their respective J_4 values being 17.6 and 13.2 Hz and $|^2J(H,H')| = 4.2$ Hz. The related data for $[IrH_2I(CO)(Et_3P)_2]$ are: δIr-H = − 10.52 and δIr-H' = − 17.50 ppm, their respective J_4 values being 18.7 and 13.9 Hz and $|^2J(H,H')| = 5.0$ Hz. [x] The hydrido-ions are not equivalent: δIr-H = − 8.22 and δIr-H' = − 17.99 ppm, their respective J_4 values being 19 and 11 Hz and $|^2J(H,H')| = 3$ Hz. [y] This resonance appears as a triplet. Thus, at room temperature the $-CH_2-$ protons appear to be equivalent. This may be a deceptively simple situation. [z] Data for a solution of $[Ir(CO)(CH_3CN)(Ph_2PCH_2Ph)_2][BF_4]$ (**24**) prepared *in situ* by bubbling H_2 through a $CDCl_3$ solution of **15** for 30 min. The hydrido-ions are not equivalent: δIr-*H* = − 9.07 and δIr-*H'* = − 18.90 ppm, their respective J_4 values being 17.5 and 12.5 Hz and $|^2J(H,H')| = 8.7$ Hz. [α] Parameters for the species produced by saturating a $CDCl_3$ solution of *trans*-[IrCl(CO)(**1**)] with CO and presumed to be $[IrCl(CO)_2$(**1**)]. [β] Parameters for the colourless species obtained by saturating $CDCl_3$ or CD_3COCD_3 solutions of *trans*-$[Ir(CO)(CH_3CN)$(**1**)] $[BF_4]$ with CO which is presumed to be $[Ir(CO)_3$(**1**)] $[BF_4]$. [γ] Parameters for the species produced by saturating a $CDCl_3$ solution of *trans*-$[Rh(CO)(CH_3CN)$(**1**)] $[BF_4]$ with CO and presumed to be $[Rh(CO)_2(CH_3CN)$(**1**)] $[BF_4]$. [δ] Broad triplet. [ε] Parameters for the species formed by adding an excess of SO_2 to a $CDCl_3$ solution of *trans*-[IrCl(CO)(**1**)].

in the ranges observed for the corresponding Ph_3P-complexes [13] and are consistent with a *trans*-geometry for the phosphorus atoms.

The IR. stretching frequencies ν_{CO} for the complexes of ligand **1** are listed in *Table 1*. As expected, their values are close to those of the corresponding complexes with Ph_2PCH_2Ph which are also listed in *Table 1*. It was not possible to make a reliable assignment of the $\tilde{\nu}_{CN}$ for complexes **7**, **12** and **15**. A weak band at 2290 cm^{-1} has been assigned to $\tilde{\nu}_{CN}$ in *trans*-$[Ir(CO)(CH_3CN)(Ph_3P)_2][ClO_4]$ [14].

2.2. *Ligand Addition Reactions of Square Planar Complexes.* As complexes *trans*-$[IrX(CO)(R_3P)_2]$ react with ligands L such as CO, R_3P and SO_2 giving five-coordinate species of the type $[IrX(L)(CO)(R_3P)_2]$, it was of interest to establish whether analogous species could be obtained from *trans*-[IrX(CO)(**1**)] and whether the presence of ligand **1** produced changes in structure and/or reactivity.

2.2.1. *Addition of Carbon Monoxide. trans*-$[IrCl(CO)(Ph_3P)_2]$ reacts with CO giving $[IrCl(CO)_2(Ph_3P)_2]$ [15] or, in the presence of $[BPh_4]^-$, giving $[Ir(CO)_3(Ph_3P)_2][BPh_4]$ [16].

The ^{31}P-NMR. spectrum of a $CDCl_3$ solution of *trans*-[IrCl(CO)(**1**)], which had been saturated with CO, showed that a single new species, **25**, had been formed. Its NMR. parameters are given in *Table 3*. This species showed $\tilde{\nu}_{CO}$ at 1930 (sh) and 1960 (*s*) cm^{-1}. As the $\tilde{\nu}_{CO}$ of $[IrCl(CO)_2(Ph_3P)_2]$ occur at 1923 (*s*) and 1976 (*vs*) cm^{-1} [15], the new species formed in solution is likely to be [IrCl(CO)$_2$(**1**)]. However, attempts to isolate this species as described for its Ph_3P-analogue [15] led to the recovery of the starting material.

Solutions of *trans*-[Ir(CO)(CH_3CN)(**1**)][BF_4], in chloroform or acetone, on addition of CO first developed a red colour and then became colourless. The ^{31}P-NMR. spectra of these colourless solutions showed that a single species, **26**, had been formed which, however, rapidly decomposed as did the solid obtained by precipitation. Elemental analysis showed that the decomposition product did not contain nitrogen. The NMR. parameters of the species present in the colourless solutions are given in *Table 3*. IR.$\tilde{\nu}_{CO}$ were found as follows: $CHCl_3$ solution, 2070 (*w*) 2020 (*s*) and 2000 (*s*) cm^{-1}; acetone solution, 1990 (*sh*) 1950 (*s*) and 1935 (*s*) cm^{-1}; solid in a nujol mull, 2075 (*w*) 2020 (*s*) and 1985 (*s*) cm^{-1}. As *Church et al.* [16] report $\tilde{\nu}_{CO}$ stretches for $[Ir(CO)_3(Ph_3P)_2][BPh_4]$ at 2074 (*w*) 2018 (*s*) and 2010 (*s*) cm^{-1}, it is presumed that [Ir(CO)$_3$(**1**)][BF_4] is formed in solution. Its decomposition, however, appears to be more complex than simple loss of CO. The transient red colour is suggestive of the formation of [Ir(CO)$_2$(**1**)][BF_4] since cationic species $[Ir(CO)_2(R_3P)_2]^+$ (R = cyclohexyl and isopropyl) have a red colour [16].

The reaction of *trans*-[Rh(CO)(CH_3CN)(**1**)][BF_4] with CO was also followed by ^{31}P-NMR. The NMR. parameters of the single species produced, **27**, are given in *Table 3*. IR.$\tilde{\nu}_{CO}$ stretches were found at 2010 (*s*) and 2045 (*m*) cm^{-1}. This compound, possibly [Rh(CO)$_2$(CH_3CN)(**1**)][BF_4], rapidly loses CO and reverts to the starting material when an inert gas is passed through the solution.

2.2.2. *Addition of Sulfur Dioxide.* The deep green solution obtained by addition of an excess of sulfur dioxide to a chloroform solution of *trans*-[IrCl(CO)(**1**)] contains a single species, **28**, with the NMR. parameters given in *Table 3*. This reaction is easily reversed and, thus, this species, which is presumed to be $[IrCl(CO)(SO_2)(\mathbf{1})]$, could not be isolated. Adducts of this type show characteristic SO_2-infrared absorptions, *e.g.*, for $[IrCl(CO)(SO_2)(Ph_3P)_2]$ the following bands have been recorded: $\tilde{\nu}_1$ (sym. str.) = 1048, $\tilde{\nu}_3$ (asym. str.) = 1198, 1185 and $\tilde{\nu}_2$ (bend) = 559 cm^{-1} [17]. The IR. spectrum of a benzene solution of *trans*-$[IrCl(CO)(\mathbf{1})]$ which had been treated with SO_2 was more complex than expected from summation of the bands of the starting material, SO_2 and the solvent, but an identification of bands arising from the presence of coordinated SO_2 could not be reliably made. Supporting evidence for the formation of $[IrCl(CO)(SO_2)(\mathbf{1})]$ is provided by the value of $\tilde{\nu}_{CO}$,which changes from 1965 cm-1 in the starting material, to 2010 cm^{-1} in the product. A similar shift is observed between *trans*-$[IrCl(CO)(Ph_3P)_2]$ and $[IrCl(CO)(SO_2)(Ph_3P)_2]$, *i.e.*, $\tilde{\nu}_{CO}$ moves from 1956 to 2020 cm^{-1} [17].

Unlike *trans*-$[RhCl(CO)(Ph_3P)_2]$ [17], *trans*-$[RhCl(CO)(\mathbf{1})]$ did not react with SO_2.

2.2.3. *Addition of Phosphines and Conclusions.* It is found that while *trans*-$[Ir(CO)(CH_3CN)(Ph_3P)_2][ClO_4]$ reacts with Ph_3P to give $[Ir(CO)(Ph_3P)_3][ClO_4]$ [14], there is no reaction between *trans*-$[Ir(CO)(CH_3CN)(\mathbf{1})][BF_4]$ and Ph_3P, presumably because of unfavourable steric interactions caused by the presence of ligand **1**.

All the above data indicate that the presence of ligand **1** in rhodium (I) and iridium (I) complexes causes a significant destabilization of the five-coordinate species relative to the four-coordinate starting materials.

2.3. *Oxidative Addition Reactions of Square planar Complexes.* One of the most characteristic reactions of complexes *trans*-$[MX(CO)(R_3P)_2]$ is oxidative addition [18] to form six-coordinate species. It is found that the general order of reactivity of the four-coordinate complexes follows the relative orders: Rh < Ir and Cl < Br < I.

As mentioned earlier, complexes containing ligand **1** are expected, on steric grounds, to decrease the tendency to form six-coordinate species. Thus, the oxidative addition reactions of complexes *trans*-$[MX(CO)(\mathbf{1})]$ with small molecules such as oxygen, halogens, hydrogen halides and hydrogen appeared worthy of investigation.

2.3.1. *Addition of Dioxygen.* The only compound for which a reaction with dioxygen was observed was *trans*-$[IrI(CO)(\mathbf{1})]$. Examination of the ^{31}P-NMR. spectrum of a benzene solution of this complex, which had been kept under 30 atm of oxygen for several hours, showed that no reaction had occurred. However, the ^{31}P-NMR. spectrum of the same solution which had been kept for 48 h under 130 atm of oxygen showed the presence of a new species ($\delta^{31}P = 0.68$ ppm, $\tilde{\nu}_{CO} = 2015$ cm^{-1}) together with the starting material ($\delta^{31}P = 14.51$ ppm, $\tilde{\nu}_{CO} = 1970$ cm^{-1}) in the approximate ratio 1:3. The formation of this species was reversible as the intensity of the 2015 cm^{-1} band decreased after passing nitrogen through the solution for several minutes. The presence of the characteristic $\tilde{\nu}_{OO}$, which is usually observed at *ca.* 850 cm^{-1} [19], could not be established with certainty as the starting material shows four bands of medium intensity at 840, 875, 900 and 920 cm^{-1} and the mixture of products obtained above shows an intense, broad absorption between 760 and 850 cm^{-1}. It has been observed that the formation of an O_2-adduct causes a shift towards high frequency of the $\tilde{\nu}_{CO}$, *e.g.*, for *trans*-$[IrI(CO)(Ph_3P)_2]$ $\tilde{\nu}_{CO} = 1975$ cm^{-1} and for

[IrI(O_2)(CO)$(Ph_3P)_2$] $\tilde{\nu}_{CO}$ = 1995 cm^{-1} [20], it is thus presumed that the new species is [IrI(O_2)(CO)(**1**)]. The pure product, however, could not be isolated.

As an equilibrium constant of 8.75×10^5 has been reported for the reaction of [IrI(CO)$(Ph_3P)_2$] with O_2 when carried out at 40° in chlorobenzene [21], it appears that complexes containing ligand **1** show a greatly reduced tendency to oxidatively add dioxygen. Considerations of the molecular structures of [IrI(O_2)(CO)$(Ph_3P)_2$] [22] and of *trans*-[RhCl(CO)(**1**)], which is isostructural with *trans*-[IrCl(CO)(**1**)] [23], indicate that significant distortions of the coordination polyhedron would be necessary to accomodate the O_2-molecule. The difficult formation of the dioxygen adduct in complexes containing ligand **1** is reflected by their activation energies. As noted earlier, an oxygen-pressure of 30 atm was insufficient for the formation of the adduct. This is to be contrasted with the uptake of oxygen by *trans*-[IrI(CO)$(Ph_3P)_2$] which occurs at atmospheric pressure with the following activation parameters: $\Delta H^{\neq} = 10.9$ kcal/mol and $\Delta S^{\neq} = -24$ e.u. [20].

2.3.2. *Addition of Halogens.* These reactions were studied only qualitatively by carrying out ^{31}P-NMR. measurements on solutions of complexes *trans*-[MX(CO)(**1**)] (M = Rh, Ir) to which halogens had been added. An immediate reaction was observed in all cases. The oxidation of the iridium(I) complexes produce mixtures of products, some of which are metastable, and are still under investigation.

The addition of chlorine to *trans*-[RhCl(CO)(**1**)] at low temperature gives a single product with $\delta^{31P} = 25.12$ ppm and $|^1J(^{103}Rh, ^{31}P)| = 72.5$ Hz, a coupling constant which is characteristic for a rhodium(III) complex [13a] containing *trans*-phosphorus atoms. This species, however, slowly reverts to the starting material [24].

2.3.3. *Addition of Hydrogen Halides.* Complexes *trans*-[IrX(CO)(**1**)] (X = Cl, Br, I) reacted smoothly with hydrogen halides to give complexes [IrHX_2(CO)(**1**)], **16–18**, which were isolated and characterized. Complex [IrHCl_2(CO)$(Ph_2PCH_2Ph)_2$], **19**, was also prepared for purposes of comparison. Their IR. spectroscopic data are given in *Table 1* and the NMR. data in *Table 3*. The latter data are indicative of structures in which the hydrogen atom is in *cis*-position to two phosphorus atoms which have a mutual *trans*-geometry. As the complexes [IrHX_2(CO)$(Ph_3P)_2$] have been assigned structures containing the same relative arrangement of hydrogen and phosphorus atoms about the metal centre, with the hydrogen atom in *trans*-position to a halogen [25], it is presumed that this configuration of donor atoms is also present in the corresponding complexes of ligand **1**. The mutual arrangement of H-, X- and CO-ligands in the Ph_3P-complexes was established on the basis of the $\tilde{\nu}_{Ir\text{-}X}$ stretches which, in the case of the chloro-complexes, were observed at *ca.* 310 cm^{-1} for Ir-Cl when chlorine was in *trans*-position to another Cl-atom and at *ca.* 265 cm^{-1} for the Ir-Cl when chlorine was in *trans*-position to CO [25]. This criterion could not be used for the assignment of geometry in complexes of ligand **1** as a number of ligand absorptions also occur in this region. Thus, for *trans*-[IrBr(CO)(**1**)], bands were found at 301 (*m*), 292 (*w*) and 272 (*mw*) cm^{-1} and the corresponding bands in *trans*-[IrI(CO)(**1**)] were observed at 300 (*m*), 292 (*w*) and 274 (*mw*) cm^{-1}. It was also found that the spectrum of *trans*-[IrCl(CO)(**1**)] showed bands at 301 (*sh*), 288 (*sh*) and 270 (*m*) cm^{-1} as well as a broad, medium strong absorption between 310 and

315 cm^{-1} which could correspond to the Ir-Cl stretch. As the IR. spectrum of $[IrHCl_2(CO)(\mathbf{1})]$ showed medium-to-weak intensity bands at 250, 270, 280, 305, 318 and 325 cm^{-1}, no reliable assignment of geometry could be made on this basis.

Complex $[RhHCl_2(CO)(\mathbf{1})]$ did not form on addition of HCl to *trans*-$[RhCl(CO)(\mathbf{1})]$: the ^{31}P-NMR. spectrum of a CD_2Cl_2 solution of the rhodium(I) complex remained unchanged after addition of gaseous HCl. The preparation of $[RhHCl_2(CO)(Ph_3P)_2]$ has been described but no details about its stability are reported [26]. However, complexes $[RhHCl_2(CO)(Ph_3A)_2]$ (A = As, Sb) [27] and $[RhHBr_2(CO)(Ph_3P)_2]$ [28] are reported as being stable only in the presence of an excess of HX.

It can then be concluded that ligand **1** allows the formation of six-coordinate species, and that the resulting complexes are inert if at least one of the donor atoms is hydrogen. Consideration of the molecular structures of complexes *trans*-$[MCl(CO)(\mathbf{1})]$ (M = Rh, Ir) [23] indicates that it is possible to fit a hydrogen ligand on the benzo[*c*]phenanthrene side of the 'plane' defined by P_1, P_2, M, Cl and CO. The failure of *trans*-$[RhCl(CO)(\mathbf{1})]$ to add HCl does, however, indicate that the presence of ligand **1** reduces the tendency towards oxidative addition even for molecules such as HX.

2.3.5. *Addition of Dihydrogen.* Complexes *trans*-$[IrI(CO)(\mathbf{1})]$ and *trans*-$[Ir(CO)(CH_3CN)(\mathbf{1})][BF_4]$ reacted with dihydrogen giving $[IrH_2I(CO)(\mathbf{1})]$ and $[IrH_2(CO)(CH_3CN)(\mathbf{1})][BF_4]$ respectively. Dihydrogen reacted also with the colourless solution formed by addition of CO to *trans*-$[Ir(CO)(CH_3CN)(\mathbf{1})][BF_4]$, which is presumed to contain $[Ir(CO)_3(\mathbf{1})][BF_4]$, to give $[IrH_2(CO)_2(\mathbf{1})][BF_4]$. These complexes could be isolated in an analytically pure state. The complexes $[IrH_2I(CO)(Ph_2PCH_2Ph)_2]$, $[IrH_2(CO)(CH_3CN)(Ph_2PCH_2Ph)_2][BF_4]$ and $[IrH_2(CO)_2(Ph_2PCH_2Ph)_2]$ were also prepared for purposes of comparison with the corresponding species containing ligand **1**. IR. data for all these complexes are given in *Table 1*. Complex $[IrH_2I(CO)(Ph_3P)_2]$ shows $\tilde{\nu}_{IrH}$ and $\tilde{\nu}_{CO}$ bands at 1987, 2045 and 2092 cm^{-1} [20] and corresponding frequencies for $[IrH_2I(CO)(Et_3P)_2]$ have been observed at 1975, 2080 and 2159 cm^{-1} [29].

The NMR. data for the hydrido-complexes of ligand **1** and of Ph_2PCH_2Ph are given in *Table 3*. The ^1H-NMR. resonances of the $-CH_2-$ groups appear as 'virtually coupled' triplets indicating a *trans*-arrangement of the phosphorus atoms. Furthermore, the values of $|^2J(^{31}P, ^1H_{hydride})|$ are 10-20 Hz indicating that the hydride ligands are in *cis*-position to the phosphorus atoms [30]. In complexes $[IrH_2I(CO)(\mathbf{1})]$ and $[IrH_2(CO)(CH_3CN)(\mathbf{1})][BF_4]$ the two hydride ligands are inequivalent and the values of $|^2J(^1H, ^1H')|$ indicate that they are mutually *cis*. Thus it is probable that their structures are related to those of complexes $[IrHX_2(CO)(\mathbf{1})]$, *i.e.*, with one hydrogen atom in *trans*-position to the halide ligand (or acetonitrile) and the other in *trans*-position to CO.

It is also found that in complex $[IrH_2(CO)_2(\mathbf{1})][BF_4]$ the two hydride ligands are magnetically equivalent suggesting a geometry in which these ligands are in *trans*-positions to carbon monoxide.

3. Conclusions.

- This study has confirmed that the static properties of square planar complexes of ligand **1** are very similar to those of the corresponding complexes with related monodentate phosphines [6]. It has also shown that the presence of ligand **1** does not prevent the formation of six-coordinate species and that compounds of this type are best obtained if at least one of the ligands is hydrogen. Finally it has been shown that square planar complexes can undergo oxidative addition reactions and that the stability of the resulting products can be significantly lower than that of the corresponding complexes with monodentate phosphines. This destabilization of the six-coordinate species confirms the predictions made on the basis of considerations of molecular models [4].

Experimental Part. - For generalities see [6]. Solvents were dried and distilled by standard methods [31] and degassed prior to use. Ligand **1** was prepared as described elsewhere [4]. Reactions involving free ligand or Ag[BF_4] were carried out in a nitrogen atmosphere. The complexes were prepared in an analytically pure state as described below.

NMR.-measurements were carried out on a *Bruker* HX-90 spectrometer operating at 36.43 MHz for ^{31}P and 90 MHz for protons and were made on $CDCl_3$ solutions unless otherwise specified.

trans-*[RhCl(CO)(*__1__*)]* (**3**). 1.30 g (2.05 mmol) **1**, in 10 ml benzene, was gradually added to a stirred solution of 0.36 g (0.93 mmol) [$Rh_2Cl_2(CO)_4$] [7] in 10 ml benzene. The yellow reaction mixture was taken to dryness under reduced pressure and the residue washed with 3 x 30 ml acetone and dried i.V.

trans-*[RhBr(CO)(*__1__*)]* (**4**). 0.10 g (0.97 mmol) NaBr, in 10 ml ethanol, was added to 0.50 g (0.57 mmol) **7**, in 30 ml acetone. The yellow precipitate was filtered off, washed with acetone and ether and dried i.V.

trans-*[RhI(CO)(*__1__*)]* (**5**). It was prepared from 0.15 g (1.04 mmol) NaI and 0.50 g (0.57 mmol) **7** as described above and purified by washing with ethanol and acetone.

trans-*[Rh(NCS)(CO)(*__1__*)]* (**6**). It was prepared from 0.10 g (1.31 mmol) NH_4NCS and 0.30 g (0.34 mmol) **7** as described above and purified by washing with acetone.

trans-*[Rh(CO)(CH₃CN)(*__1__*)][BF₄]* (**7**). A solution of 0.29 g (1.5 mmol) $AgBF_4$ in 3 ml CH_3CN was added to a suspension of 1.13 g (1.5 mmol) **3** in 20 ml CH_3CN. The mixture was stirred for 24 h and the solvent evaporated under reduced pressure. The residue was extracted with 20 ml acetone and the extract filtered through a small column packed with 2.0 g silica gel which had been covered with 0.5 g celite. The column was washed with 25 ml acetone and the solution evaporated under reduced pressure. The pure complex was obtained by slow evaporation of an acetone solution of the crude product in a stream of nitrogen and the solid thus obtained dried i.V.

trans-*[IrCl(CO)(*__1__*)]* (**8**). - *Method A.* A solution of 0.80 g $IrCl_3 \cdot xH_2O$ (x = 5.75, 2 mmol) in 90 ml 2-methoxyethanol and 10 ml water were refluxed in a stream of CO until a pale yellow solution was obtained (*ca.* 6 h). 1.75 g (2.1 mmol) **1** was then added and the solution allowed to cool down slowly in a stream of CO. The yellow precipitate was filtered off, washed 3 times with 30 ml acetone and dried i.V. (Yield 80-90%). - *Method B.* A solution of 1.75 g **1** (2.1 mmol) in 20 ml benzene was added to a stirred solution of 0.74 g (2 mmol) [$IrCl(CO)_2(p\text{-}CH_3 \cdot C_6H_4 \cdot NH_2)$] [8] in 100 ml benzene. The yellow solid obtained by evaporation of the solvent under reduced pressure was washed 4 times with 50 ml ether and dried i.V. (Yield 85%). - *Method C.* 0.45 g (0.75 mmol) **1** in 40 ml acetone was added to a stirred solution of 0.50 g (0.71 mmol) [Ph_4As][$IrCl_2(CO)_2$] [9] in 20 ml acetone and the yellow suspension stirred overnight. The precipitate was filtered off, washed twice with 20 ml ethanol and 3 times with 20 ml ether and dried i.V. (Yield 80%).

trans-*[IrBr(CO)(*__1__*)]* (**9**), trans-*[IrI(CO)(*__1__*)]* (**10**), trans-*[Ir(NCS)(CO)(*__1__*)]* (**11**) *and* trans-*[Ir(CO)(CH₃CN)(*__1__*)][BF₄]* (**12**) were prepared and purified as described for their rhodium analogues.

trans-*[RhCl(CO)(Ph₂PCH₂Ph)₂]* (**13**). It was prepared as described for **3** and recrystallized from $CHCl_3$/ethanol.

trans-*[IrCl(CO)(Ph₂PCH₂Ph)₂]* (**14**). It was prepared and purified as described for **8** using method B.

trans-*[Ir(CO)(CH₃CN)(Ph₂PCH₂Ph)₂][BF₄]* (**15**). It was prepared as described for **12**. The crude product was recrystallized from methanol.

*[IrHCl₂(CO)(*__1__*)]* (**16**). An approximate twofold excess of HCl in benzene was added to a stirred solution of 0.22 g (0.25 mmol) **8** in 20 ml benzene. The solvent was evaporated to a small volume under reduced pressure, the crystals filtered off, washed with acetone and dried i.V.

*[IrHBr₂(CO)(*__1__*)]* (**17**). The stoichiometric quantity of 65% aq. HBr-solution in 5 ml acetone was added to a stirred solution of 0.23 g (0.25 mmol) **9** in 15 ml $CHCl_3$. The solvent was evaporated under

reduced pressure and the crude product recrystallized by slow evaporation of a CH_2Cl_2 solution and dried i.V.

[IrHI$_2$(CO)(**1**)*]* (**18**). It was prepared from **10** and aq. HI-solution as described above for **17**.

[IrHCl$_2$(CO)(Ph$_2$PCH$_2$Ph)$_2$] (**19**). It was obtained from $IrCl_3$ and the phosphine using Method A described for **8**. The product was recrystallized from CH_2Cl_2 and dried i.V.

[IrH$_2$I(CO)(**1**)*]* (**20**). Hydrogen was bubbled through a solution of 0.10 g (8 mmol) **10** in 10 ml CH_2Cl_2 for *ca.* 4 h. The product crystallized out from the resulting very pale yellow solution by slow addition of ether.

[IrH$_2$(CO)(CH$_3$CN)(**1**)*][BF$_4$]* (**21**). Hydrogen was bubbled through a solution of 0.10 g (3 mmol) of **12** in 10 ml of CH_2Cl_2 for *ca.* 4 h. A layer of ether was floated over the top of the colourless solution and the mixture was kept for 3 days at $-5°$. The product was filtered off and dried i.V.

[IrH$_2$(CO)$_2$(**1**)*][BF$_4$]* (**22**). CO was bubbled through a solution of 0.10 g (0.1 mmol) **12** in 3 ml acetone until it became pale yellow. Hydrogen was then bubbled through this solution for *ca.* 5 min. The product was obtained from the colourless solution as described above for **21**.

[IrH$_2$(CO)$_2$(Ph$_2$PCH$_2$Ph)$_2$][BF$_4$] (**23**). It was prepared and purified as described above for **22**.

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