220. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. VII[1]). The Preparation of the Five-Coordinate Complexes $[M(CO)_3(\mathbf{1})]$ (M = Fe, Ru; (1) = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene)

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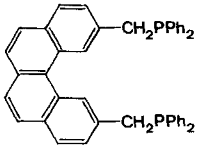
Summary

The five-coordinate mononuclear complexes $[M(CO)_3(\mathbf{1})]$ (M = Fe, Ru; (1) = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene) have been prepared and assigned trigonal bipyramidal structures with apical phosphorus atoms from IR. and NMR. data.

1. Introduction. - During a study of the coordinating properties of the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) it was shown that this ligand easily formed complexes with square-planar coordination [2]. It was also shown that ligand (**1**) allowed the isolation of six-coordinate species [3], while five-coordinate complexes containing ligand **1**, *e.g.*, $[IrCl(CO)_2(\mathbf{1})]$ and $[Ir(CO)_3(\mathbf{1})][BF_4]$, could be detected only in solution. As it has been reported [4] that five-coordinate complexes of the type $[M(CO)_3(R_3P)_2]$ (M = Fe(O), Ru(O)), unlike those derived from complexes of the type $[MX(CO)(R_3P)_2]$ (M = Rh(I), Ir(I)) [5], do not tend to become four-coordinate, the preparation of complexes $[M(CO)_3(\mathbf{1})]$ (M = Fe(O), Ru(O)) was undertaken.



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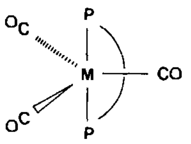

2 M = Fe
4 M = Ru

2. Results and discussion. - Complexes of the type $[Fe(CO)_3L_2]$ (L = tertiary phosphine) have been prepared either by direct substitution of carbon monoxide in iron carbonyl complexes [6] or by replacement of a diolefin in $[Fe(CO)_3$(*diolefin*)] [7]. The complex $[Fe(CO)_3(\mathbf{1})]$ (**2**) was best prepared by the thermal reaction of $[Fe(CO)_3(C_8H_8)]$ [7] with **1** in 1,2-dimethylcyclohexane. Complex **2** can also be

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[1]) Part VI, see [1].

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prepared (a) by the photochemical reaction of [Fe(CO)$_3$(C$_4$H$_6$)] [8] with ligand **1** and (b) by the reaction of [Fe*(acac)*$_3$] *(acac = acetyl-acetonate)* with (*iso*-Bu)$_3$Al, **1** and carbon monoxide in analogy to the method of *Kubo et al.* [9].

It is noteworthy that: (i) **2** is also produced by the reaction of [FeI$_2$(CO)$_4$] [10] with **1** and (ii) **1** does not displace triphenylphosphine from [Fe(CO)$_3$(Ph$_3$P)$_2$] [7]. For spectral comparison [Fe(CO)$_3$ (Ph$_2$PCH$_2$Ph)$_2$] (**3**), was also prepared, the best preparative method being thermal reaction of the phosphine with [Fe(CO)$_3$(C$_8$H$_8$)].

The complex [Ru(CO)$_3$(**1**)] (**4**) was also best prepared from the tricarbonyl-cyclooctatetraene compound, *i.e.*, [Ru(CO)$_3$(C$_8$H$_8$)], but, in contrast to the corresponding iron compound, the reaction required photochemical activation. Complex **4**, however, could not be obtained either by phosphine exchange starting from [Ru(CO)$_3$ (Ph$_3$P)$_2$] [11] or from the reaction of [RuCl$_2$(C$_7$H$_8$)]$_n$ with carbon monoxide, hydrazine hydrate and **1**, as described by *Kapoor & King* [11] for the monodentate phosphine system.

The complex [Ru(CO)$_3$(Ph$_2$PCH$_2$Ph)$_2$] (**5**) required for spectral comparison, was prepared from [Ru(CO)$_3$(C$_8$H$_8$)] but could also be obtained in low yield by the method of *Kapoor & King* [11]. The yellow, crystalline, monomeric complexes **2**, **3**, **4** and **5** are air-stable, but their solutions, particularly those of the ruthenium complexes, are oxygen-sensitive. They show moderate to good solubilities in aromatic and chlorinated hydrocarbon solvents.

Significant IR. and NMR. data for **2**–**5** and ^{31}P-NMR. and IR. data for compounds [M(CO)$_3$(Ph$_3$P)$_2$] (M = Fe, Ru) are given in the *Table.*

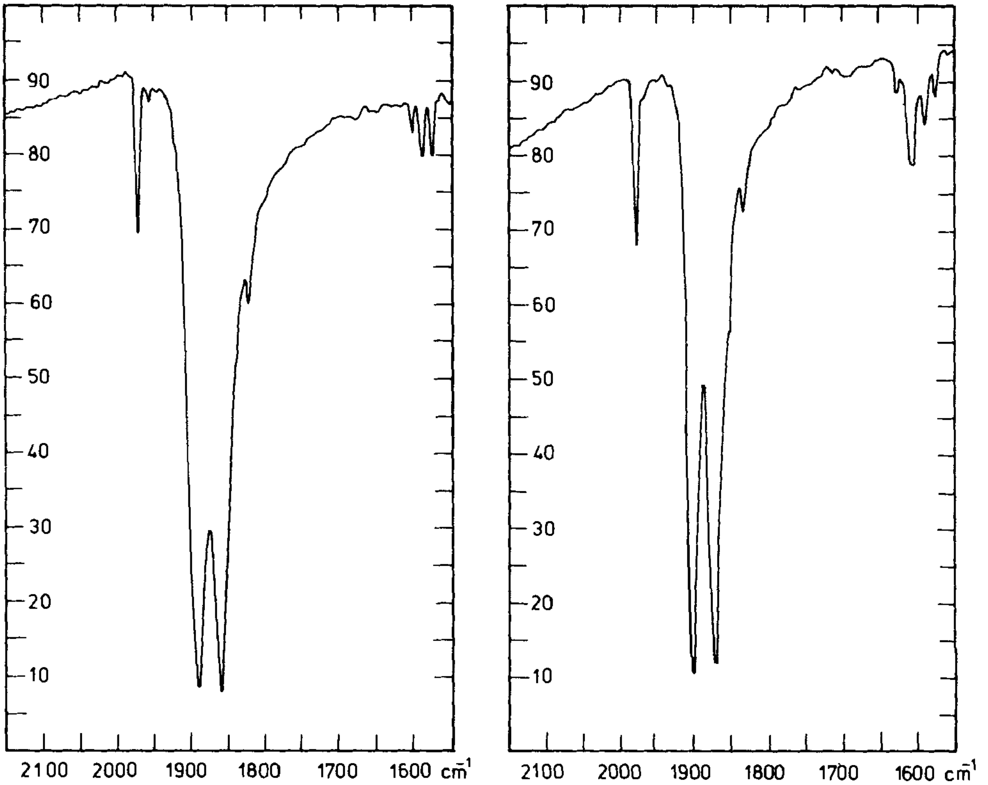
As expected, **2** and **4** are five-coordinate. It was not possible to carry out their crystal structure determination as suitable crystals could not be obtained. However, these compounds are assigned a trigonal bipyramidal structure, with apical phosphorus atoms, on the basis of their IR. and ^{31}P-NMR. spectra.

All complexes of the type [Fe(CO)$_3$L$_2$] (L = R$_3$P, (RO)$_3$P) have also been assigned trigonal bipyramidal structures with apical phosphorus atoms [12]. Although many of these complexes show three bands in the CO-stretching region, it is postulated that in these cases the D_{3h}-microsymmetry is still present. Thus *Bigorgne et al.* [13] report the appearance of a split E′-mode and of a forbidden A$_1'$-band in [Fe(CO)$_3${P(OMe)$_3$}$_2$], which are attributed to internal ligand asymmetry. The X-ray structure [14] clearly shows both the D_{3h}-microsymmetry and the

Table

	^{31}P-NMR.	^{1}H-NMR.		IR.
	δ^{31}P [ppm][a]	δ-CH$_2$-[ppm]	J[b] [Hz]	$\tilde{\nu}_{CO}$ [cm^{-1}]
[Fe(CO)$_3$(Ph$_3$P)$_2$][c]	82.3	–	–	1882[d]
[Fe(CO)$_3$(**1**)]	76.1[e]	4.19	9.1	1869, 1898, 1976[f]
[Fe(CO)$_3$(Ph$_2$PCH$_2$Ph)$_2$]	81.6[e]	3.87	8.8	1858, 1888, 1967[f]
[Ru(CO)$_3$(Ph$_3$P)$_2$[g]	55.4	–	–	1900[d]
[Ru(CO)$_3$(**1**)]	49.5	4.16	8.2	1880, 1910, 1980[i]
[Ru(CO)$_3$(Ph$_2$PCH$_2$Ph)$_2$]	54.2[h]	3.84	7.6	1872, 1900, 1970[i]

[a] Relative to H$_3$PO$_4$ with a positive value indicating a shift to lower field. [b] $J = |^2J_{PH} + ^4J_{PH}|$. [c] See Ref. 7. [d] Measured in CHCl$_3$ solution. [e] Measured in acetone with C$_6$D$_6$ capillary. [f] Measured in a Nujol mull. [g] See Ref. 11. [h] Measured in C$_6$D$_6$. [i] Measured in KBr disk.



[$Fe(CO)_3(Ph_2PCH_2Ph)_2$]

[$Fe(CO)_3$(1)]

Figure. *1550–2200 cm^{-1} region of the IR. spectra of [$Fe(CO)_3(Ph_2PCH_2Ph)_2$] and [$Fe(CO)_3$* (**1**)*]*

internal ligand asymmetry of the phosphite molecule. The observation of three bands in the CO-stretching region of [$M(CO)_3(Ph_2PCH_2Ph)_2$] (M = Fe, Ru) is thus consistent with D_{3h}-microsymmetry. The band-splitting observed is to be expected in view of the low symmetry of the phosphine ligand.

As the IR. spectra of **2** and **4** are practically identical with those of **3** and **5** respectively (see *Table* and *Fig.*) we deduce that the phosphorus atoms of ligand **1** occupy apical positions in a trigonal bipyramidal structure, as observed in [RuCl(CO)(NO)(**1**)] [15].

Additional support is provided by the ^{31}P-NMR. spectra of complexes [$M(CO)_3L_2$] (M = Fe, Ru; L = Ph_3P, Ph_2PCH_2Ph; L_2 = **1**), where the δ^{31}P values of the iron and ruthenium series are strictly comparable *(Table)*.

Interesting information is also obtainable from the ^{1}H-NMR. spectra of the benzylic protons. In **2** and **3** the signals appear as 'filled up' doublets [16] while in **4** and **5** 'triplets' are observed. The pattern depends on the magnitude of the P-P-coupling [17]. Thus for large ^2J(P,P) values *pseudo*-triplets are observed while for small ^2J(P,P) values *pseudo*-doublets appear in the spectrum. When ^2J(P,P) has intermediate values 'filled-up doublets' result.

The *pseudo*-triplets shown by **4** and **5** are consistent with the expected large value of ${}^2J$(P,P) arising from the presence of a metal centre of the second transition series [16] and of *trans*-phosphorus atoms [17]. The 'filled-up doublets' shown by **2** and **3** are also in agreement with the proposed structure if one takes into account that for complexes of the same type ${}^2J$(P,P) values are smaller in the first than in the second transition series [16].

3. Experimental Part. - For generalities see [2]. NMR.-measurements were carried out on a *Bruker* HX90 spectrometer operating at 36.43 MHz for ^{31}P and 90 MHz for ^{1}H and were made on $CDCl_3$ solutions under N_2 unless otherwise specified. IR. spectra were recorded on a *Beckman* IR4250 Spectrophotometer in the range 4000-200 cm^{-1}. Elemental analyses and molecular weight determinations were performed by the Microanalytical Laboratory of the ETH Zürich. The UV.-activated reactions were carried out with a *Philips* 125 Watt middle-pressure mercury-UV.-lamp. Solvents were dried and distilled by standard methods [18] and degassed before use. Ligand **1** was prepared as described elsewhere [19] and Ph_2PCH_2Ph was prepared as described below. *All manipulations were carried out in a N_2 atmosphere.* The decomposition-points were measured on a *Büchi* melting point-apparatus after Dr. *Tottoli.*

The compounds were prepared in an analytically pure state as described below.

Ph_2PCH_2Ph. 25 g (0.095 mol) Ph_3P was added to a solution of 4.36 g (0.19 mol) sodium in 400 ml liquid ammonia. 5.09 g (0.095 mol) NH_4Cl was then slowly added, and after 15 min the mixture was treated with 17 g (0.10 mol) benzylbromide dissolved in 30 ml degassed ether. After evaporating the ammonia the product was dried and washed with water, ethanol and acetone. White crystals of m.p. 74°. Yield: 85%.

$C_{19}H_{17}P$					
	Calc.	C 82.41	H 6.29	P 11.23%	(M.W. 276.32)
	Found	„ 82.59	„ 6.20	„ 11.21%	(M.W. 276)

*[Fe(CO)$_3$(**1**)]* (**2**). - a) 35 mg (0.18 mmol) [$Fe(CO)_3(C_4H_6)$] and 100 mg (0.16 mmol) **1** were stirred in 10 ml benzene for 16 h with UV. irradiation. After evaporating the solvent i.V. the product was dissolved in CH_2Cl_2 and eluted on a column (neutral alumina) with light petroleum (b.p. 30-60°). Yellow crystals of dec. p. 230-235°. Yield: 80%.

b) 122 mg (0.5 mmol) [$Fe(CO)_3(C_8H_8)$] [7] and 156 mg (0.25 mmol) **1** in 5 ml 1,2-dimethylcyclohexane were heated with stirring at 100° for 17 h. The precipitate was filtered off and purified by column chromatography as described under a). Yield: 62%.

c) 200 mg (0.32 mmol) **1**, in 3 ml toluene, was added to a stirred solution of 112 mg (0.32 mmol) [Fe(*acac*)$_3$] in 10 ml ether. The mixture was cooled to – 70°, and 150 mg (0.96 mmol) (*iso*-Bu)$_3$Al very slowly added while CO was bubbled through the solution. The solution was allowed to warm-up over 3 h (during which time reaction occurred). The product was filtered off and purified as described above. Yield: 21%.

$C_{47}H_{34}O_3P_2Fe$					
	Calc.	C 73.83	H 4.48	P 8.10%	(M.W. 764.59)
	Found	„ 73.56	„ 4.60	„ 7.94%	(M.W. 759)

[Fe(CO)$_3$(Ph$_2$PCH$_2$Ph)$_2$] (**3**). 244 mg (1 mmol) [$Fe(CO)_3(C_8H_8)$] and 276 mg (1 mmol) Ph_2PCH_2Ph in 10 ml 1,2-dimethylcyclohexane were stirred for 15 h at 100°. The solid obtained on cooling this solution, was filtered off and purified as described for **2**. Pale yellow crystals of dec. p. 195-200°. Yield: 45%.

$C_{41}H_{34}O_3P_2Fe$						
	Calc.	C 71.11	H 4.95	P 8.94	Fe 8.06	(M.W. 692.47)
	Found	„ 71.00	„ 4.94	„ 8.78	„ 8.33	

*[Ru(CO)$_3$(**1**)]* (**4**). - a) 0.75 g (1.17 mmol) [$Ru_3(CO)_{12}$] and 3.0 g (28.8 mmol) C_8H_8 were stirred in 25 ml cyclohexane and irradiated with UV. light while CO was bubbled through the solution. The residue obtained by evaporation of the solvent was extracted with hexane and the extract evaporated to dryness. The crude product thus obtained was sublimed at 0.5 Torr and 60°. Orange-yellow crystals of [$Ru(CO)_3(C_8H_8)$] were obtained. Yield: 35%.

b) A stirred solution of 400 mg (0.64 mmol) **1** and 170 mg (0.58 mmol) $[Ru(CO)_3(C_8H_8)]$ in 65 ml acetone/toluene 12:1 was irradiated with UV. light. The crude product obtained by evaporation of the solvent i.V. was purified as described for **2**. Yield: 68%. Pale yellow crystals of dec. p. 210°.

$C_{47}H_{34}O_3P_2Ru$	Calc.	C 69.71	H 4.23	P 7.65%	(M.W. 809.81)
	Found	„ 69.40	„ 4.44	„ 7.57%	(M.W. 823)

$[Ru(CO)_3(Ph_2PCH_2Ph)_2]$ (**5**). A suspension of 0.6 g (2.27 mmol) $[RuCl_2(C_7H_8)]_n$ [20], 2 ml hydrazine hydrate and 0.84 g (3.05 mmol) Ph_2PCH_2Ph in 100 ml ethanol was refluxed for 6 h while CO was bubbled through the mixture. The precipitate was purified as described above. Yellow crystals of dec. p. 178°. Yield: 10%.

$C_{41}H_{34}O_3P_2Ru$	Calc.	C 66.75	H 4.65	P 8.40%	(M.W. 737.74)
	Found	„ 66.82	„ 4.64	„ 7.63%	(M.W. 734)

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REFERENCES

[1] *P.N. Kapoor & L.M. Venanzi,* Helv. *60,* 2824 (1977).
[2] *N.J. DeStefano, D.K. Johnson & L.M. Venanzi,* Helv. *59,* 2683 (1976).
[3] *F.J.S. Reed & L.M. Venanzi,* Helv. *60,* 2804 (1977).
[4] 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands', Ed. C.A. McAuliffe, McMillan, London 1973.
[5] *L. Vaska & S.S. Bath,* J. Amer. chem. Soc. *88,* 1333 (1966).
[6] *F.T. Delbeke, G.P. Van der Kelen & Z. Eeckhaut,* J. organomet. Chemistry *16,* 512 (1969).
[7] *T.A. Manuel & F.G.A. Stone,* J. Amer. chem. Soc. *82,* 366 (1960).
[8] *F.J.S. Reed & L.M. Venanzi,* unpublished observations.
[9] *Y. Kubo et al.,* J. organomet. Chemistry *84,* 369 (1975).
[10] *W. Hieber & G. Bader,* Chem. Ber. *61,* 1720 (1928).
[11] *P.N. Kapoor & R.B. King,* Inorg. Chemistry *11,* 336 (1972).
[12] *A. Reckziegel & M. Bigorgne,* J. organomet. Chemistry *3,* 341 (1965).
[13] *M. Bigorgne et al.,* Spectrochim. Acta *26A,* 1217 (1970).
[14] *D. Ginderow,* Acta crystallogr. *B30,* 2798 (1974).
[15] *R. Holderegger, L.M. Venanzi, F. Bachechi, P. Mura & L. Zambonelli,* Helv. *62,* 2159 (1979).
[16] *J.G. Verkade,* Co-ord. chem. Rev. *9,* 1 (1972/73).
[17] *J.F. Nixon & A. Pidcock,* 'Annual Rev. of NMR Spectroscopy', *Vol. 2,* 345 (1969).
[18] *D.D. Perrin, W.F.L. Amarego & D.R. Perrin,* 'The Purification of Laboratory Chemicals', Pergamon Press, New York 1966.
[19] *N.J. De Stefano, D.K. Johnson, R.M. Lane & L.M. Venanzi,* Helv. *59,* 2674 (1976).
[20] *E.W. Abel, M.A. Bennett & G. Wilkinson,* J. chem. Soc. *1959,* 3178.