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Alkyl and Aryl Compounds of Iridium and Rhodium. XXII*. Preparation and Fluxional Behaviour of Some Tris(diphenylphosphinomethyl)ethane Derived Organoiridium and -Rhodium Complexes [MeC(CH$_2$-PPh$_2$)$_3$]M(R)(CO)

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A number of complexes of the form [MeC(CH$_2$-PPh$_2$)$_3$]M(R)(CO) (M = Ir: R = Me, CH$_2$CMe$_3$, CH$_2$SiMe$_3$, Ph; M = Rh: R = CH$_2$SiMe$_3$) have been prepared from [MeC(CH$_2$PPh$_2$)$_3$]MCl(CO) and the respective organolithium reagent. These compounds are fluxional at ambient temperatures but stereochemically rigid on the NMR time scale at low temperatures. In the slow exchange limit, the ^{31}P NMR spectra are AK$_2$ (M = Ir) or AK$_2$X (M = Rh) patterns which define the solution state stereochemistry of the complexes as trigonal bipyramidal. As the temperature is raised, the spectra broaden in the transition region and become a single line (M = Ir) or a doublet (M = Rh) in the fast exchange limit. Conceptually, the rearrangements observed for this class of fluxional organometallic molecules are most simply viewed as turnstile rotations.

Introduction

In a recent communication [1], we have described a series of triphosphine derived organoiridium(I) complexes (*chel*-P$_3$)Ir(R)(CO), where *chel*-P$_3$ represents one of the tridentate ligands PhP(CH$_2$CH$_2$-PPh$_2$)$_2$, PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$, and MeP(CH$_2$CH$_2$-CH$_2$PPh$_2$)$_2$. According to ^{31}P NMR, these five-coordinate compounds are stereochemically rigid at ambient temperatures. This property most probably results from geometric constraints produced by the chelating ethylene- or trimethylene-linked oligophosphines: these will generally span P–M–P angles close to 90°, *i.e.* axial-equatorial sites in a trigonal bipyramid or basal-basal positions in a square pyramid [2, 3]. On passing from the respective ground-state configurations to the diequatorial or apical-basal intermediate structures of an arbitrary intramolecular permutational isomerization process the chelates must open to P_{eq}–M–P_{eq} and P_{ap}–M–P_{ba} angles of approximately 120 and 105° [4], respectively. Strain thus develops, thereby substantially raising the barrier to rearrangement [1, 3].

In this paper we report on some formally analogous iridium and rhodium species (TDPME)-M(R)(CO), where TDPME = tris(diphenylphosphinomethyl)ethane, MeC(CH$_2$PPh$_2$)$_3$, and R = alkyl or phenyl. These compounds have been prepared with the objective of examining whether the TDPME ligand is linked to the metal atom in a *cis*-bidentate or in a *fac*-tridentate fashion, thus giving rise to stereochemically rigid or non-rigid four- or five-coordinate complexes. Stereochemical rigidity may be anticipated for *cis*-planar molecules of formulation [Ph$_2$PCH$_2$(Me)C(CH$_2$PPh$_2$)$_2$]M(R)(CO) since the closely related platinum complex *cis*-[Ph$_2$PCH$_2$-(Me)C(CH$_2$PPh$_2$)$_2$]PtMe$_2$ [5] has been shown not to exchange its bonded and nonbonded phosphine groups up to *ca.* 85 °C [6]. On the other hand, rapid intramolecular equilibration of the PPh$_2$ substituents of the TDPME ligand has been demonstrated for (TDPME)Ni(C$_2$F$_4$) [7] as well as for several cobalt derivatives of composition [(TDPME)Co(CO)(L)]X (L = phosphine, phosphite; X$^-$ = BF$_4^-$, PF$_6^-$) [8] all of which contain tripodal tridentate TDPME.

Experimental

General Procedures and Instrumentation

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to recommended procedures and were distilled under nitrogen prior to use. Infrared spectra of KBr pellets of the compounds were recorded on a Perkin Elmer 325 spectrometer. ^{31}P NMR spectra were collected in THF on a Bruker WH 90 instrument operating at 36.44 MHz. The spectra were referenced to external H$_3$PO$_4$ (downfield positive).

Preparation of Complexes

(TDPME)Ir(Me)(CO) (I)

A solution of 6.0 mmol of methyllithium in 3.5 ml of diethyl ether was slowly added to a suspension of 1.76 g (2.0 mmol) of (TDPME)IrCl(CO) [9] in 200 ml of THF. This mixture was stirred at room temperature for 15 min and then filtered and concentrated *in vacuo* to *ca.* 100 ml. Ethanol (100 ml) was subsequently added and the resultant solution was evaporated until the point of precipitation of **I** was reached. Cooling to 0 °C gave a total

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TABLE I. IR and ^{31}P NMR Data of (TDPME)Ir(R)(CO), R = Me (I), CH_2CMe_3 (II), CH_2SiMe_3 (III), Ph (IV), and (TDPME)Rh(CH_2SiMe_3)(CO) (V).[a]

Compd.	IR ν(CO)	^{31}P NMR fast exchange limit[b]	^{31}P NMR slow exchange limit[c]		
	(cm^{-1})	$\delta(^{31}P)$	$\delta(^{31}P_{ax})$	$\delta(^{31}P_{eq})$	^2J(PP) [Hz]
I	1860	−19.5s	−12.9t	−21.4d	25
II	1854	−22.8s	−17.6t	−26.0d	27
III	1861	−22.1s	−14.6t	−26.0d	26
IV	1879	−19.9s	−9.6t	−22.8d	28
V	1877	6.9d[d]	20.0dt[e]	0,5dd[f]	40

[a] For sampling details *cf.* 'Experimental'. [b] Ambient temperatures (*ca.* 35 °C); s = single line; d = doublet. [c] I, II: T = −83 °C; III: T = −63 °C; IV: T = −90 °C; V: T = −73 °C; t = triplet. [d] ^1J(RhP) = 109 Hz. [e] ^1J(RhP) = 86 Hz. [f] ^1J(RhP) = 120 Hz.

of 1.23 g (72%) of **I** as yellow crystals which were washed with ethanol (3 × 10 ml) and dried *in vacuo.* Found: C, 60.6; H, 5.4; P, 10.7; calcd. for $C_{43}H_{42}IrOP_3$ (859.9): C, 60.06; H, 4.92; P, 10.81%.

(TDPME)Ir(CH₂CMe₃)(CO) (II)

By analogy to compound **I** from 2.0 mmol of (TDPME)IrCl(CO) and 6.0 mmol of Me_3CCH_2Li in 300 ml of diethyl ether (6 h at room temperature). Yield: 1.50 g (82%) of yellow complex **II**. Found: C, 61.6; H, 5.6; P, 10.8; calcd. for $C_{47}H_{50}IrOP_3$ (916.0): C, 61.63; H, 5.50; P, 10.14%.

(TDPME)Ir(CH₂SiMe₃)(CO) (III)

As described above from 2.0 mmol of starting chloro complex and 6.0 mmol of Me_3SiCH_2Li in 300 ml of Et_2O (6 h at room temperature). Yield: 1.55 g (83%) of yellow crystals. Found: C, 59.1; H, 5.4; P, 10.0; calcd. for $C_{46}H_{50}IrOP_3Si$ (932.1): C, 59.27; H, 5.41; P, 9.97%.

(TDPME)Ir(Ph)(CO) (IV)

Similar to **I–III** from 2.0 mmol of (TDPME)IrCl(CO) and 6.0 mmol of phenyllithium in 300 ml of ether (3 h at room temperature). Yield: 1.40 g (76%) of **IV** as yellow crystals. Found: C, 62.8; H, 5.0; P, 9.6; calcd. for $C_{48}H_{44}IrOP_3$ (922.0): C, 62.53; H, 4.81; P, 10.08%.

(TDPME)Rh(CH₂SiMe₃)(CO) (V)

As described for the iridium complexes from 1.58 g (2.0 mmol) of (TDPME)RhCl(CO) [9] and 6.0 mmol of Me_3SiCH_2Li in 300 ml of Et_2O (4 h at room temperature). Yield: 1.21 g (72%) of a brownish yellow powder. Found: C, 65.1; H, 6.1; P, 11.2; calcd. for $C_{46}H_{50}OP_3RhSi$ (842.8): C, 65.56; H, 5.98; P, 11.03%.

Results and Discussion

Treatment of the chloro compounds (TDPME)MCl(CO) (M = Ir, Rh) [9] in THF or Et_2O solution with an excess of organolithium reagents LiR yielded air-sensitive yellow complexes of composition (TDPME)M(R)(CO); M = Ir: R = Me (**I**), CH_2CMe_3 (**II**), CH_2SiMe_3 (**III**), Ph (**IV**); M = Rh: R = CH_2SiMe_3 (**V**).

The low carbonyl absorptions of **I–V**, <1900 cm^{-1} (Table I), are in accord with those expected for a five-coordinate structure [1, 9, 10]. The alternative geometry, in which the central metal is four-coordinate and TDPMe behaves as a bidentate ligand occupying *cis* positions, would be anticipated to give rise to ν(CO) bands in the 1920–1980 cm^{-1} region [11–14].

Two idealized geometries, the trigonal bipyramid and the square pyramid, have previously been established for triphosphine derived pentacoordinate d^8 complexes by X-ray diffraction [2]. In view of the peculiarity of tridentate TDPME to chelate to metal centers in a facial arrangement, trigonal bipyramidal (TDPME)M(R)(CO) complexes would exhibit in the slow exchange limit AB_2 or AK_2 ^{31}P NMR patterns for M = Ir and $\mathbf{AB_2X}$ or $\mathbf{AK_2X}$ spectra for M = Rh. A square pyramidal stereochemistry would give ABC or related first-order splittings for the iridium compounds and **ABCX** or comparable first-order patterns for the rhodium species. For all the complexes described herein the slow exchange limiting ^{31}P NMR spectra have been obtained at temperatures between −63 and −90 °C and they all correspond to the trigonal bipyramidal structure (Table I), in which the CO ligand is assigned to an equatorial site because of the better back-bonding in that position [4]. This stereochemistry should be rather distorted since formation of the idealized trigonal bipyramidal structure would require the diequatorial P–M–P chelate angles to approach 120°. Due to the constrained nature of the TDPME ligand the backbone of this triphosphine will, however, generally bridge P–M–P angles of, at best, 95–97° only [6, 8].

As the temperature is raised, the doublet/triplet patterns of the phosphorus-31 spectra of **I–V** begin to broaden and eventually collapse into a single line

(M = Ir; A_3 spectrum) or into a sharp doublet (M = Rh; A_3X spectrum). The value of $^1J(^{103}Rh-^{31}P)$ in the high temperature limit, 109 Hz, is equal to the weighted average of the low temperature limit coupling constants $^1J(^{103}Rh-^{31}P_{eq})$, 120 Hz, and $^1J(^{103}Rh-^{31}P_{ax})$, 86 Hz.

The maintenance of rhodium-to-phosphorus coupling at ambient temperatures indicates that magnetic equivalence of the phosphine groups is achieved through either an intramolecular nonbond-breaking permutational rearrangement, or an intramolecular dissociative process comprising M–P bond-breaking and bond-forming via short-lived 'arm off' intermediates, or an intermolecular process involving exchange of the neutral carbonyl ligand [15]. Since no reaction of **I–V** was observed with methyl iodide to form methyl phosphonium iodide derivatives, reversible dissociation of the PPh_2 substituents was deemed the least probable of the three alternatives [7]. Intermolecular processes leading to rearranged molecules through exchange of the CO ligand were likewise excluded because the NMR behaviour of the complexes studied in this paper remained invariant to trace amounts of added trimethyl phosphite. This finding is consistent with results previously reported by Meek [8], according to which intermolecular carbonyl exchange is very slow for the stereochemically-related $[(TDPME)Co(CO)(L)]^+$ cations.

It would therefore seem likely that positional exchange of the phosphorus atoms of **I–V** occurs through an intramolecular nonbond-breaking isomerization. For the following two reasons the turnstile rotation [16] conceptually provides a satisfactory explanation for the observed non-rigidity of the (TDPME)M(R)(CO) complexes: (1) trigonal bipyramidal coordination compounds of the TDPME ligand may be viewed as transition metal analogues of the stereochemically closely related caged oxyphosphoranes $X(CH_2O)_3P(OCY)_2$ (X = MeC, P; Y = CH_3, CF_3), the facile rearrangements of which have been suggested to present definite examples of turnstile motions [16]; (2) the first step of the turnstile mechanism involves a compression of the diequatorial angle in the rotating trio from the ideal 120° to 90° which with respect to the steric constraints of the tripod ligand appears to be an attractive motion within the [(TDPME)M] fragments.

When contrasted with the non-fluxional nature of $RP[(CH_2)_nPR_2]$ derived species such as, *e.g.*, $[MeP(CH_2CH_2CH_2PPh_2)_2]Ir(R)(CO)$, $[PhP(CH_2CH_2CH_2PPh_2)_2]Ir(R)(CO)$ [1], and $[PhP(CH_2CH_2PPh_2)_2Co(CO)(L)]^+$ [8], the fluxionality of five-coordinate complexes of TDPMe may be attributed to the C_{3v} symmetry of the *fac*-$[MeC(CH_2PPh_2)_3M]$ moieties which renders the effects of ring strain inoperative.

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