Inorganica Chimica Acta, 114 (1986) 95–99

Preparation and Characterisation of Ni(II), Pd(II) and Pt(II) Complexes of 1-Diphenylphosphino-2-bis(*m*-trifluoromethylphenyl)phosphinoethane, (*m*-CF_3P–P)

PRAMESH N. KAPOOR* and P. C. MERCYKUTTY

Department of Chemistry, University of Delhi, Delhi 110007, India

Received October 16, 1985

Abstract

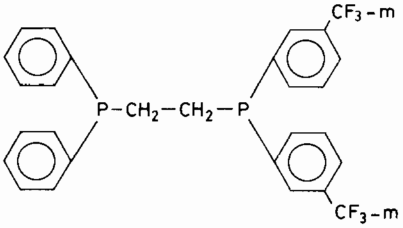
A series of four-coordinate, square-planar, diamagnetic 1-diphenylphosphino-bis(*m*-trifluoromethylphenyl)phosphinoethane complexes of type *cis*-[MX_2(*m*-CF_3P–P)] (M = Ni, Pd, Pt; X = Cl, Br, I or NCS) have been prepared. These complexes have been characterized by $^{31}P\{^1H\}$ NMR, ^1H NMR, IR and UV spectroscopy, elemental analyses and magnetic susceptibility measurements. The effects of various substituents on the phenyl groups of the ditertiary phosphines on the solubility characteristics of the metal complexes are discussed.

Introduction

The coordination chemistry of the symmetrical ditertiary phosphines, $R_2PCH_2CH_2PR_2$, is well documented and is dominated by the formation of stable five-membered ring chelate complexes [1–6]. Ten-membered ring binuclear complexes have also been reported recently [7]. In a few cases, these also behave as monodentate or bridging ligands, and have been used in the synthesis of heterobimetallic complexes [8–10].

In contrast to the above, few metal complexes of unsymmetrical ditertiary phosphines have been reported [11–14]. Studies of these unsymmetrical ditertiary phosphines are of considerable interest, since they contain in the same molecule, two phosphorus atoms which are magnetically non-equivalent, thus demonstrating the potential of ^{31}P NMR studies as a probe of stereochemical behaviour of the resulting transition-metal complexes [14–16].

Although the ditertiary phosphine ($Ph_2PCH_2CH_2PPh_2$) complexes of Ni(II), Pd(II) and Pt(II) were reported about two decades ago [17, 18], few attempts have been made [12, 19, 20] to study unsymmetrical ditertiary phosphines containing electronegative substituents on the phosphorus atoms. In an earlier publication [14], we reported the Ni(II), Pd(II) and Pt(II) complexes of two unsymmetrical ditertiary phosphines (*p*- or *m*-FC_6H_4)$_2$-$PCH_2CH_2PPh_2$. This paper describes an analogous series of Ni, Pd and Pt complexes of the ditertiary phosphine ligand (*m*-CF_3P–P), the synthesis of which was reported earlier [21].



(m-CF_3P–P)

Experimental

Physical measurements and experimental techniques were carried out as described elsewhere [14].

Synthesis of Complexes

1. [Ni(m-CF_3P–P)Cl_2]

$NiCl_2 \cdot 6H_2O$ (0.19 g, 0.78 mmol) dissolved in butan-1-ol (30 ml) was refluxed for 1 h to produce a light green solution. To this, 1-diphenylphosphino-2-bis(*m*-trifluoromethylphenyl)phosphinoethane (0.42 g, 0.78 mmol) was added, giving a deep red solution. The reaction mixture was then refluxed for 2 h. On cooling, red crystals were deposited which were collected on a sintered glass crucible and crystallized from a mixture of methylene chloride and n-hexane.

2. [Ni(m-CF_3P–P)Br_2]

This complex was prepared as described above, $NiBr_2$ being used. Recrystallization of the crude

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

TABLE I. Some Physical Properties, Elemental Analyses, IR and UV Data

Compound	Colour	Melting point (decomp.) (°C)	%C	%H	%P	ν(M–X) (cm^{-1})	(nm) in acetone
[Ni(m-CF_3P–P)Cl_2]	Red	219–221	50.64[a] (50.38)	3.34 (3.10)	9.33 (9.02)	328, 352	456
[Ni(m-CF_3P–P)Br_2]	Brown	228–229	44.66 (44.23)	2.95 (2.71)	8.23 (7.96)	275, 300	488
[Ni(m-CF_3P–P)I_2]	Mauve	239–241	39.71 (39.39)	2.62 (2.25)	7.32 (6.98)	–	530
[Ni(m-CF_3P–P)$(NCS)_2$]	Yellow	234–236	50.80 (50.45)	3.13 (2.91)	8.74 (8.42)	–	436
[Pd(m-CF_3P–P)Cl_2]	Light yellow	273–275	47.23 (46.91)	3.12 (2.90)	8.70 (8.36)	290, 305	
[Pd(m-CF_3P–P)Br_2]	Yellow	264–265	41.99 (41.56)	2.77 (2.39)	7.74 (7.39)	246, 270	
[Pd(m-CF_3P–P)I_2]	Yellow	268–270	37.58 (37.23)	2.48 (2.26)	6.92 (6.58)	–	
[Pd(m-CF_3P–P)$(NCS)_2$]	Yellow	168–170	47.58 (47.33)	2.93 (2.71)	8.18 (7.93)	–	
[Pt(m-CF_3P–P)Cl_2]	White	276–277	42.01 (41.86)	2.77 (2.55)	7.74 (7.52)	300, 320	
[Pt(m-CF_3P–P)Br_2]	Light yellow	209–211	37.81 (37.63)	2.49 (2.26)	6.97 (6.76)	235, 285	
[Pt(m-CF_3P–P)I_2]	Light yellow	281–282	34.19 (34.02)	2.26 (2.13)	6.30 (6.21)		

[a]Calc. (Found).

product from a mixture of methylene chloride and n-hexane gave brown crystals.

3. [Ni(m-CF_3P–P)I_2]

A solution of NiI_2 was freshly prepared by refluxing $Ni(NO_3)_2 \cdot 6H_2O$ (0.2 g, 1.01 mmol) and KI (0.54 g, 3.20 mmol) in butan-1-ol (30 ml) for 2 h. The solution was cooled and filtered, and the filtrate was again refluxed for 1 h. To this, the ligand (m-CF_3P–P′) (0.39 g, 0.73 mmol) was added. The solution became mauve in colour. On cooling, mauve-coloured crystals were deposited, which were collected and crystallized as for the bromide.

4. [Ni(m-CF_3P–P)$(NCS)_2$]

This complex was prepared as in the case of the iodo analogue, KSCN being used in the place of KI.

5. [Pd(m-CF_3P–P′)Cl_2]

Palladium dichloride (0.29 g, 1.65 mmol) dissolved in acetonitrile (40 ml) was refluxed for 4 h to produce a brown solution. To this, (m-CF_3P–P′) (0.88 g, 1.65 mmol) was added and the reaction mixture was refluxed for a further 3 h. The grey product obtained after the removal of the solvent was then purified by treating with charcoal in refluxing methylene chloride. On drying, a light yellow product was obtained which was crystallized from $CHCl_3$ and n-hexane.

6. [Pd(m-CF_3P–P)X_2] (X = Br, I or NCS)

These complexes were obtained by metathetical exchange reactions, treating [Pd(m-CF_3P–P′)Cl_2] with an excess of the corresponding potassium or ammonium salt in boiling acetone. The resulting complexes were filtered, dried and extracted with CH_2Cl_2.

7. [Pt(m-CF_3P–P)Cl_2]

Dichlorobis(benzonitrile)platinum(II), [Pt(PhCN)$_2Cl_2$] (0.45 g, 0.94 mmol) was treated with (m-CF_3P–P) (0.50 g, 0.94 mmol) in refluxing benzene (30 ml) or chloroform at 60 °C for about 10 h. The initial yellow colour gradually turns light yellow and finally colourless. The white product thus obtained was dried under vacuum and was crystallized from CH_2Cl_2 and EtOH to give the pure white crystalline compound.

8. [Pt(m-CF_3P–P)X_2] (X = Br or I)

These complexes were prepared by metathetical exchange reactions using the same procedure adopted for the palladium complexes. The resulting complexes were crystallized from $CHCl_3$ and petroleum ether.

Results and Discussion

The complexes were prepared as described in the experimental section. Some of their physical

TABLE II. $^{31}P\{^1H\}$ NMR Parameters for the Complexes of Ni(II), Pd(II) and Pt(II) obtained at 80.98 MHz in $CDCl_3$ at 25 ℃

Compound	Chemical shift (ppm)		Coordination chemical shift (ppm)		$J(P-P')$ (Hz)	ΔR (ring coordination)[d]	
	δPPh_2	$\delta P(m\text{-}CF_3C_6H_4)_2$	ΔPPh_2	$\Delta p(m\text{-}CF_3C_6H_4)_2$		ΔPPh_2	$\Delta P(m\text{-}CF_3C_6H_4)_2$
$[Ni(m\text{-}CF_3P-P)Cl_2]$	+54.35	+54.86	+66.55	+66.06	39.85		
$[Ni(m\text{-}CF_3P-P)Br_2]$	+61.12	+63.65	+73.32	+74.85	40.92		
$[Ni(m\text{-}CF_3P-P)I_2]$	+76.14	+78.60	+88.34	+89.80	40.23		
$[Ni(m\text{-}CF_3P-P)(NCS)_2]$	a						
$[Pd(m\text{-}CF_3P-P)Cl_2]$	+61.22	+62.83	+73.42	+74.03	9.14	+30.72	+31.33
$[Pd(m\text{-}CF_3P-P)Br_2]$	+63.52	+65.42	+75.72	+76.62	15.27	+33.02	+33.92
$[Pd(m\text{-}CF_3P-P)I_2]$	+58.99	+61.46	+71.19	+72.66	13.43	+28.49	+29.96
$[Pd(m\text{-}CF_3P-P)(NCS)_2]$	+65.50	+66.30	+77.70	+77.50	b	+35.00	+34.80
$[Pt(m\text{-}CF_3P-P)Cl_2]$[c]	+41.79	+42.14	+53.99	+53.34	3.77	+31.69	+31.04
$[Pt(m\text{-}CF_3P-P)Br_2]$	a						
$[Pt(m\text{-}CF_3P-P)I_2]$	a						

[a] Chemical shifts could not be obtained due to low solubility of the complex. [b] $J(P-P')$ could not be observed due to broad peaks. [c] $J(^{195}Pt-^{31}PPh_2)$ = 3574.07 Hz and $J(^{195}Pt-^{31}P(C_6H_4F_3C\text{-}m)_2)$ = 3659.72 Hz. [d] R = Coordination chemical shift of the chelate complex – coordination chemical shift of non-chelate complex Δ*cis*-$[Pd\{P(Ph_2Et)_3\}_2Cl_2]$ = 42.70 and Δ*cis*-$[Pt\{P(Ph_2Et)_3\}_2Cl_2]$ = 22.30 (ref. 35).

characteristics and analytical data are given in Table I.

It is noteworthy that the presence of a CF_3 group in *m*-position on the terminal phenyl substituents of the ligand (m-CF_3-P–P) results in the formation of complexes which are soluble in hydroxylic solvents, while the presence of a CH_3 group, also in *m*-position, in the ligands significantly increases the solubility of their complexes in hydrocarbon solvents [13]. Similar observations were also reported [22] in the case of Ni(II), Pd(II) and Pt(II) complexes of the ligand, 2,11-bis(diarylphosphinomethyl)benzo[C]-phenanthrene(aryl=*m*-tolyl and m-$CF_3C_6H_4$).

The ^{31}P NMR parameters obtained for the complexes prepared are listed in Table II, which provides both gross and subtle structural information. The main features of the $^{31}P\{^1H\}$ NMR spectra are closely related to those observed for analogous complexes of the ditertiary phosphines, (*m*- or *p*-$FC_6H_4)_2PCH_2CH_2PPh_2$ [14]. The analysis of the AB spectra observed for the ligand [21] and its complexes indicates that the appearance of the spectra is markedly dependent on the relative values of the spin–spin couplings $J(P-P')$ and the chemical shift difference between the two non-equivalent phosphorus nuclei $\nu_0\delta$. Many factors are known to strongly influence the magnitude of $J(P-P)$ [23, 24], including the nature of the transition metal, the ligands other than phosphorus in the complex, and the substituents bonded to the phosphorus. It is assumed that $|J_{PP'}$ obs.$|$ in these complexes includes a major contribution from coupling through the metal atom (^2J-PMP′) rather than from ligand backbone coupling ($J_{PP'}$B); this explains the observed decrease in the $|J_{PP'}$obs.$|$ values down the series Ni > Pd > Pt (Table II).

The $^{31}P\{^1H\}$ NMR spectra of the platinum complexes are characterized by the presence of two satellites due to $^{195}Pt-^{31}P$ and $^{195}Pt-^{31}P'$ couplings. The magnitude of $^{195}Pt-^{31}P$ coupling constants is usually considered to be dominated by the Fermi-contact term, which is directly proportional to valence s orbital contribution at the respective nuclei and to direct or indirect bonding of the two nuclei; this has been discussed in detail [14]. As expected, the $^{31}P\{^1H\}$ NMR spectrum of the complex $[Pt(m\text{-}CF_3P-P')Cl_2]$ showed two coupling constants, 3659.72 Hz and 3574.07 Hz, and confirmed the *cis*-configuration of the complex. It has been shown that the electron withdrawing ability of the substituents attached to the phosphorus nucleus has a marked influence on the coupling constants [24–26]. Allen *et al.* [25] have shown that the $^1J(^{195}Pt-^{31}P)$ coupling constants in a series of heteroaryl- and triaryl-phosphines towards Pt(II) increased as the groups attached to phosphorus became more electron-withdrawing, indicating an s character for the phosphorus lone-pair orbital involved in bonding to platinum, in accordance with Bent's rule [27].

Similar arguments have been made by Hill and coworkers [28], who found that the Pt–P coupling constants for the complexes containing the *cis* chelating ligands $(C_6H_5)_2P[B_{10}H_{10}C_2]PRR'$ increase with the electronegativity of the substituents on phosphorus (*i.e.*, $P(C_6H_5)_2 < P(C_6F_5)_2 < P(NMe_2)_2 < P(F)NMe_2$). Since a larger Pt–P coupling has been observed for shorter Pt–P bond distances and the Pt–P stretching frequencies in the infrared also increase in the same order as the $^1J_{Pt-P}$ values, they have suggested that the Pt–P bond strength increases in the same order [19]. The increased Pt–P bond strength is expected since the $d\pi \rightarrow d\pi$ interaction between the metal and the phosphorus donor is enhanced by the substituents with higher electronegativity on the phosphorus atom [29, 30] Such back donation would also increase the σ-bond character of the Pt–P bond by a synergistic effect [30], and this increase would account for the observed trend of the ${}^1J_{\text{Pt–P}}$ values [31, 32]. The particularly strong Pt–$P(m\text{-}CF_3C_6H_4)_2$ bond is expected to strengthen the *trans*-Pt–X bond. Thus, the donor centre $P(m\text{-}CF_3C_6H_4)_2$ has a smaller *trans* influence than the donor centre $P(C_6H_5)_2$, and ${}^1J_{PtP(m\text{-}CF_3C_6H_4)_2} > {}^1J_{PtP(C_6H_5)_2}$. These observations are in agreement with other reports [19]. The strong electron-withdrawing property of the $m\text{-}CF_3C_6H_4$ group indicates that the coupling constants 3659.72 Hz and 3574.07 Hz observed in the Pt(II) chloride complex may be assigned to $J({}^{195}Pt\text{–}{}^{31}P(C_6H_4F_3C\text{-}m)_2)$ and $J({}^{195}Pt\text{–}{}^{31}PPh_2)$, respectively. Thus, the order of coupling constants in the series $P(C_6H_5)_2 < P(p\text{-}FC_6H_4)_2 < P(m\text{-}FC_6H_4)_2 < P(m\text{-}CF_3C_6H_4)_2$ can also be explained; the order of *trans* effect is $C_6H_5 > p\text{-}FC_6H_4 > m\text{-}FC_6H_4 > m\text{-}CF_3C_6H_4$.

Investigations have shown [33] that phosphorus atoms present in 5-membered rings exhibit anomalously large coordination chemical shifts, Δ; this can be explained on the basis of ring contribution (ΔR), which is the difference between the coordination chemical shift, Δ, of a chelate complex and of the *cis*-substituted equivalent non-chelate complex. The values of ΔR for the Pd(II) and Pt(II) complexes studied have been calculated (Table II).

The ${}^1H$ NMR spectra of these complexes are not very informative and show a downfield shift of the aromatic and methylene resonances compared to those of the free ligand. The spectra exhibit an expected multiplet at ~8.4–7.26 ppm, due to phenyl protons and two overlapping triplets at ~1.20–2.62 ppm, which clearly indicate the non-equivalence of the two methylene groups in the bridge of $(C_6H_5)_2PCH_2CH_2P(C_6H_4F_3C\text{-}m)_2$.

The far IR data listed in Table I are consistent with the C_{2v} symmetry of the molecule and exhibit two infrared-active M–X vibrations indicative of *cis* geometry. The chelating nature of the ligand was confirmed by the presence of a sharp band at ~885 cm^{-1} in all the complexes prepared. An increase in frequency and intensity of the P-aryl grouping at ~1095 cm^{-1} in the complexes is a clear indication for the coordination of phosphorus to metal. In the case of thiocyanate complexes, the appearance of a strong band at ~2080 cm^{-1} confirms that the thoicyanato group is bound to the metal through the nitrogen atom (M–NCS). These reports are in close agreement with those for similar systems [14].

The electronic spectral data for the nickel complexes in acetone (Table I) show the presence of an intense band in the 400–500 nm region, consistent with a square-planar geometry. These bands move to lower energy in the order $NCS^- > Cl^- > Br^- > I^-$, showing the presence of N-bonded thiocyanate groups; two S-bonded groups would produce the order $Cl^- > Br^- > SCN^- > I^-$ [34]. The absorptions may be due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. The nickel iodide complex exhibits square-planar ⇌ tetrahedral equilibrium.

Acknowledgements

The author M.P.C. thanks CAS (UGC) New Delhi, for financial support of this work as a Junior research fellow. P.N.K. is thankful to Royal Society of Chemistry, London, for a research grant and Johnson Matthey & Co., London, for a gift of platinum salt. We are grateful to Prof. M. A. Bennett of Australian National University, Canberra and Prof. Werner Marty of Institut de Chimie, Université de Neuchâtel, Switzerland, for recording the ${}^{31}P$ NMR spectra.

References

1 W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem., 14,* 173 (1972).
2 J. A. Connor, J. P. Day, E. M. Jones and G. K. McEwen, *J. Chem. Soc., Dalton Trans.,* 347 (1973).
3 S. O. Grim. J. DelGaudio, R. P. Molenda, C. A. Tolman and J. P. Jesson, *J. Am. Chem. Soc., 96,* 3416 (1974).
4 R. B. King and J. C. Cloyd, Jr., *Inorg. Chem., 14,* 1550 (1975).
5 C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Elements', Elsevier, New York, 1979.
6 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem. Soc., Dalton Trans.,* 969 (1984).
7 J. A. Iggo and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 1009 (1985).
8 J. A. Connor, G. A. Hudson, *J. Organomet. Chem., 73,* 351 (1974).
9 R. L. Keiter, K. M. Fasig and L. W. Cary, *Inorg. Chem., 13,* 201 (1974); *14,* 201 (1975).
10 R. L. Keiter, S. K. Keiter, N. P. Hansen, J. W. Brodack and L. W. Cary, *Inorg. Chem., 20,* 283 (1981).
11 J. Bailey, M. J. Church and M. J. Mays, *J. Coord. Chem., 3,* 63 (1973).
12 L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano and L. M. Vallarino, *J. Chem. Soc., Chem. Commun.,* 999 (1974).
13 N. D. Sadanani, A. Walia, P. N. Kapoor and R. N. Kapoor, *Aust. J. Chem., 32,* 1143 (1979).
14 P. N. Kapoor, R. N. Kapoor, D. D. Pathak and G. Gaur, *Inorg. Chim. Acta, 112,* 153 (1986).
15 S. O. Grim, R. C. Barth, J. D. Mitchell and J. D. Gaudio, *Inorg. Chem., 16,* 1776 (1977).
16 F. R. Benn, J. C. Briggs and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.,* 293 (1984).
17 G. Booth and J. Chatt, *J. Chem. Soc.,* 3238 (1965).

18 G. R. Van Hecke and W. D. Horrocks, *Inorg. Chem., 5,* 1968 (1966).

19 I. Macleoud, L. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp and R. Walker, *J. Organomet. Chem., 97,* C7 (1975).

20 L. D. Brown, S. Datta, J. K. Kouba, L. K. Smith and S. S. Wreford, *Inorg. Chem., 17,* 729 (1978).

21 P. N. Kapoor, D. D. Pathak, G. Gaur and M. Kutty, *J. Organomet. Chem., 276,* 167 (1984).

22 P. N. Kapoor, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta, 65,* 654 (1982).

23 P. S. Pregosin, R. W. Kunz, *NMR Basic Prin. Prog., 16,* 28 (1979).

24 M. Pankowski, W. Chodkiewiez and M. P. Simonnin, *Inorg. Chem., 24,* 533 (1985).

25 D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.,* 51 (1982).

26 D. W. Allen, L. A. March and I. W. Nowell, *J. Chem. Soc., Dalton Trans.,* 483 (1984).

27 H. A. Bent, *Chem. Rev., 61,* 275 (1961).

28 W. E. Hill, B. G. Rackley and L. M. Silva-Trivino, *Inorg. Chim. Acta, 75,* 51 (1983).

29 S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem., 6,* 1133 (1967).

30 S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc., 89,* 5573 (1967).

31 J. A. Pople and D. P. Santry, *Mol. Phys., 8,* 1 (1964).

32 J. F. Nixon and A. Pidcock, *Ann. Rep. NMR Spectrosc., 2,* 345 (1969).

33 C. A. Tolman, *J. Am. Chem. Soc., 92,* 2953 (1970).

34 D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Am. Chem. Soc., 92,* 5351 (1970).

35 P. E. Garrou, *Chem. Rev., 81,* 229 (1981).