1,2-Bis(arylimino)propylpalladium Complexes as *N*-Donor Chelate Ligands Towards Metals of the First Transition Series

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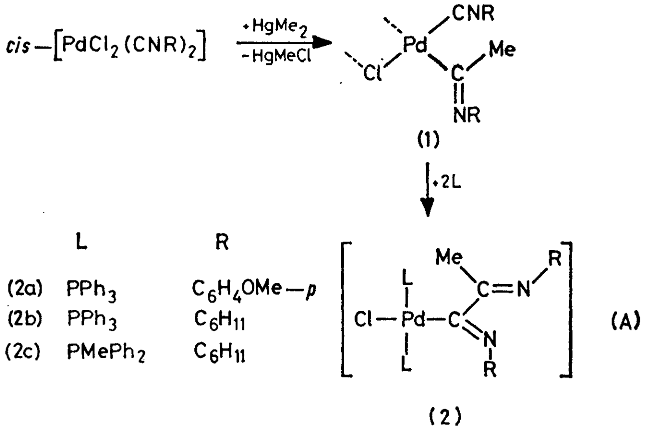
1,2-Bis(arylimino)propylpalladium(II) complexes of the type *trans*-[PdX{C(NR)CMe(NR)}L_2] (X = Cl or Br; R = C_6H_4OMe-*p* or C_6H_{11}; L = PPh_3 or $PMePh_2$) and *cis*-[PdCl{C(NC_6H_4OMe-*p*)CMe(NC_6H_4OMe-*p*)}(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) react with anhydrous metal halides, MX_2 (X = Cl or Br; M = Fe, Co, Ni, Cu, or Zn) to give 1 : 1 adducts in which the 1,2-bis(arylimino)propyl group acts as a chelating bidentate ligand. These monomeric adducts are paramagnetic (high spin) except for the diamagnetic zinc derivatives. Their electronic spectra in the visible and near-i.r. region indicate a tetrahedral configuration for M. This configuration also accords with the solid-state magnetic moments and with the Mössbauer spectrum of the $FeCl_2$ derivative.

THE nitrogen atoms of iminomethyl groups bound (*via* carbon) to transition metals have a pronounced nucleophilic character as indicated by their ease of protonation and methylation (a general synthetic route to carbene derivatives) [1-8] and their ability to act as nitrogen-donor ligands towards different metal atoms.[9,10] We have recently described the preparation of a series of palladium(II) complexes containing 1,2-bis(arylimino)propyl groups, *trans*-[PdX{C(NR)CMe(NR)}$(PPh_3)_2$] (X = Cl or I; R = Ph, C_6H_4Me-*p*, or -C_6H_4OMe-*p*) and their ready protonation at nitrogen by perchloric acid.[11] The tendency of organic α-di-imines to act as bidentate chelating ligands has prompted us to study the co-ordination properties of these palladium(II) derivatives towards a variety of transition metals. Following our short communication,[12] we now report in detail the results of our investigation using halides of metals of the first transition series.

RESULTS AND DISCUSSION

Preparation of the 1,2-*Bis*(*arylimino*)*propylpalladium Ligands* (2).—The derivatives (2) were prepared by reactions (A) in benzene. These reactions have already been discussed in detail for aromatic isocyanides and L = PPh_3.[11] We have now investigated the influence



(1)

(2)

(A)

	L	R
(2a)	PPh_3	C_6H_4OMe—*p*
(2b)	PPh_3	C_6H_{11}
(2c)	$PMePh_2$	C_6H_{11}

of the substituent R and the ligand L on the second step of reaction (A), *i.e.* (1) going to (2). The chloride-bridged complexes (1) show, in benzene solution, a strong i.r. band at *ca.* 2 200 cm^{-1} [ν(CN)]. After treat-

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[1] B. Crociani and T. Boschi, *J. Organometallic Chem.*, 1970, **24**, C1.

[2] P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Comm.*, 1970, 1627.

[3] B. Crociani, T. Boschi, and M. Nicolini, *J. Organometallic Chem.*, 1971, **33**, C81.

[4] M. F. Lappert and A. J. Oliver, *J.C.S. Chem. Comm.*, 1972, 2761.

[5] J. E. Perks and A. L. Balch, *J. Organometallic Chem.*, 1974, **71**, 453.

[6] D. F. Christian and W. R. Roper, *J. Organometallic Chem.*, 1974, **80**, C35.

[7] G. Minghetti and F. Bonati, *Inorg. Chem.*, 1974, **13**, 1600.

[8] D. R. Christian, H. C. Clark, and R. F. Stepaniek, *J. Organometallic Chem.*, 1976, **112**, 227.

[9] F. Bonati and G. Minghetti, *J. Organometallic Chem.*, 1973, **60**, C43.

[10] G. Minghetti, F. Bonati, and G. Banditelli, *Inorg. Chem.*, 1976, **15**, 2649.

[11] B. Crociani, M. Nicolini, and R. L. Richards, *J. Organometallic Chem.*, 1976, **104**, 259.

[12] B. Crociani, M. Nicolini, and R. L. Richards, *J. Organometallic Chem.*, 1976, **113**, C22.

TABLE 1

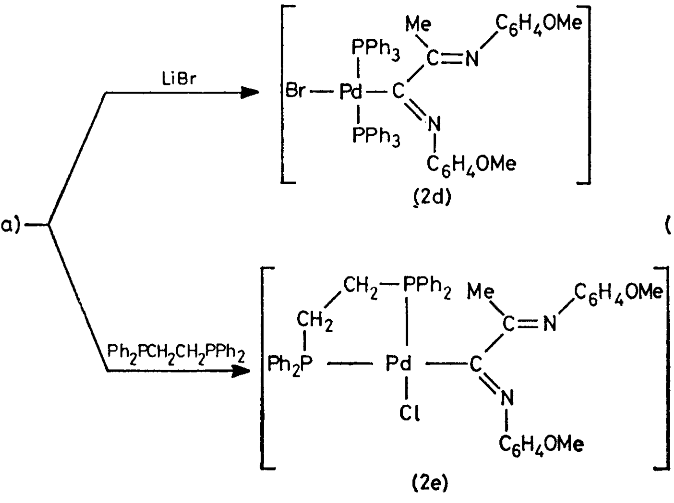
Analytical and physical data

Complex	Colour	M.p.[a] (θ_c/°C)	Analyses[b] (%) C	H	N	X	M[b]	$\mu_{eff.}$/ B.M.
$[FeCl_2(2a)]$[c]	Red-brown	172—175	59.0 (59.25)	4.60 (4.40)	2.60 (2.60)	9.9 (9.90)	1 071 (1 074.5)	5.18
$[CoCl_2(2a)]$	Red-brown	200—205	59.1 (59.05)	4.40 (4.40)	2.60 (2.60)	10.0 (9.85)	992 (1 077)	4.36
$[NiCl_2(2a)]$	Yellow-brown	194—200	58.5 (59.1)	4.40 (4.40)	2.60 (2.60)	9.90 (9.85)	1 250 (1 077)	3.24
$[CuCl_2(2a)]$	Brown	144—146	58.3 (58.80)	4.40 (4.40)	2.60 (2.60)	10.0 (9.85)	1 147 (1 082)	1.94
$[ZnCl_2(2a)]$	Yellow-orange	188—195	58.3 (58.7)	4.40 (4.35)	2.60 (2.60)	9.90 (9.80)	1 115 (1 083)	
$[PdBr\{C(NC_6H_4OMe\text{-}p)CMe(NC_6H_4OMe\text{-}p)\}(PPh_3)_2]$ (2d)	Yellow	195—203	63.7 (64.15)	4.80 (4.75)	2.70 (2.80)	8.20 (8.05)		
$[CoBr_2(2d)]$	Red-brown	194—200	53.1 (52.55)	3.80 (3.90)	2.30 (2.30)	19.7 (19.8)	1 229 (1 211)	4.70
$[ZnBr_2(2d)]$	Deep yellow	171	52.2 (52.3)	3.70 (3.90)	2.30 (2.30)	19.8 (19.7)	1 133 (1 217)	
$[PdCl\{C(NC_6H_4OMe\text{-}p)CMe(NC_6H_4OMe\text{-}p\{(dppe)]$ (2e)	Yellow	180—185	63.0 (62.85)	4.90 (5.05)	3.40 (3.40)	4.50 (4.30)		
$[CoCl_2(2e)]$	Red-brown	185	54.4 (54.3)	4.40 (4.35)	2.80 (2.95)	11.0 (11.2)	1 040 (951)	4.80
$[NiCl_2(2e)]$	Yellow-brown	195—200	53.9 (54.3)	4.40 (4.35)	2.90 (2.95)	11.0 (11.2)	1 298 (951)	3.40
$[CuCl_2(2e)]$	Brown	118—123	53.9 (54.0)	4.20 (4.30)	2.80 (2.95)	11.2 (11.1)	968 (956)	1.80
$[ZnCl_2(2e)$	Deep yellow	186	54.1 (53.9)	4.40 (4.30)	2.90 (2.95)	11.0 (11.1)	980 (958)	
$[PdCl\{C(NC_6H_{11})CMe(NC_6H_{11})\{(PPh_3)_2]$ (2b)	Pale yellow	163	67.9 (68.05)	6.10 (6.15)	3.00 (3.10)	4.00 (3.95)	*d*	
$[CoCl_2(2b)]\cdot0.25CH_2Cl_2$	Turquoise	222—229	58.5 (58.4)	5.30 (5.30)	2.70 (2.65)	11.6 (11.75)	*d*	4.19
$[NiCl_2(2b)]\cdot0.33CH_2Cl_2$	Flesh	230	58.0 (58.7)	5.30 (5.30)	2.50 (2.65)	12.4 (12.30)	*d*	3.01
$[CuCl_2(2b)]\cdot0.25CH_2Cl_2$	Orange	166—172	58.0 (58.15)	5.30 (5.30)	2.50 (2.55)	11.6 (11.7)	*d*	1.95
$[ZnCl_2(2b)]\cdot0.25CH_2Cl_2$	Pale yellow	230—245	58.4 (58.15)	5.40 (5.30)	2.60 (2.65)	11.85 (11.75)	*d*	
$[CoCl_2(2c)]$[e]	Greenish	167	54.0 (54.4)	5.60 (5.70)	3.10 (3.70)	12.0 (11.75)	1 023 (905.5)	4.41
$[CuCl_2(2c)]$[e]	Yellow-orange	139	53.9 (54.1)	5.50 (5.65)	3.00 (3.10)	11.8 (11.7)	900 (910)	1.94

[a] Uncorrected values; all the complexes decompose on melting. [b] Calculated values are given in parentheses. [c] The preparation of (2a) is already published, see ref. 11. [d] Insufficiently soluble (see text). [e] (2c) = $[PdCl\{CNC_6H_{11})CMe(NC_6H_{11})\}(PMePh_2)_2]$.

ment of (1) with L(Pd : L mol ratio = 1 : 2) this band shifts to lower wavenumber by 5—10 cm^{-1}, indicating bridge cleavage, then decreases in intensity and eventually disappears, as the co-ordinated isocyanide inserts into the σ bond between palladium and the monoimine group. The rate of the latter reaction is almost independent of the ligands L, but depends noticeably on the nature of R. For R = C_6H_4OMe-*p* the reaction is complete in *ca.* 15 min at 20 °C, while for R = C_6H_{11} the reaction time is *ca.* 90 min at 20 °C. This differing reactivity is probably due to the higher electrophilic character of the terminal carbon of co-ordinated *p*-$MeOC_6H_4NC$ as compared to $C_6H_{11}NC$; similar behaviour has been observed in insertion reactions into palladium–alkyl or –vinyl σ bonds.[13]

The other derivatives (2) were prepared from complex (2a) by substitution or metathetical reactions [equation (B)]. Complexes (2) have been characterised by elemental analysis (Table 1) and by i.r. and ^1H n.m.r. spectra (Table 2).



(B)

Preparation of Binuclear Complexes.—Derivatives (2) react with anhydrous first-row transition-metal halides according to (C) (R = C_6H_4OMe-*p* or C_6H_{11}; M = Fe, Co, Ni, or Zn; X = Cl or Br). This reaction also gives 1 : 1 adducts even when an excess of the ligand (2) is used, probably because of the steric effect of its

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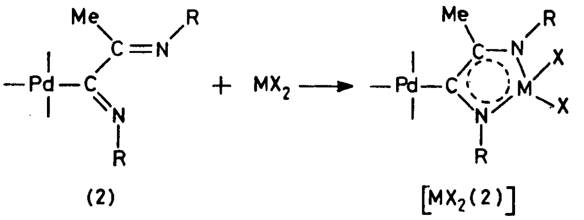
[13] S. Otsuka and K. Ateke, *J.C.S. Dalton*, 1976, 327.

bulk. Complex formation by organic 1,2-bis(arylimino)-propyl derivatives is also sensitive to steric interference, since although the ligand MeN=CR–CR=NMe (R = H or Me) easily forms 1 : 3 complexes with Fe^{II} and Ni^{II},[14,15] the N-phenyl analogue forms only a partially dissociated 1 : 2 adduct with FeCl$_2$.[16] The colour of the complexes [MX$_2$(2)] [Table 1 and equation (C)] depends markedly



(C)

on the nature of the N-substituent R and is discussed later (see Electronic Spectra).

The various ligands (2) examined have, in general, rather similar co-ordinating abilities. Ligand (2a) gives well characterised adducts [MCl$_2$(2a)], soluble in halogenated solvents, for all the metal chlorides examined. Complexes of its bromide analogue, (2d), with CoBr$_2$ and ZnBr$_2$ have been prepared in order to unambiguously assign metal–halogen stretching frequencies in the far-i.r. spectra. No well defined product was obtained with CuBr$_2$.

TABLE 2

Infrared (cm^{-1}) and ^{1}H n.m.r. spectra

Complex	Characteristic i.r. bands			^{1}H N.m.r. resonances [a]						
	ν(C=N)	ν(Pd–X)	ν(M–X)	PPh	C_6H_4	OMe	CMe	NCH	$(CH_2)_5$	Others
(2a)	1 616 (sh) 1 555m	265m		8.0—7.0 (m) [32]	6.9—6.6 (m) [4] 6.2—6.0 (m) [2]	3.88 (s) [3] 3.83 (s) [3]	1.29 (s) [3]			
[FeCl$_2$(2a)]	1 588mw	302m	358ms 327m							
[CoCl$_2$(2a)]	1 580 (sh)	301m	348s 335 (sh)							
[NiCl$_2$(2a)]	1 580 (sh)	298m	342ms 330 (sh)							
[CuCl$_2$(2a)]	1 580 (sh)	299m or 295 (sh)	329m 299m or 295 (sh)							
[ZnCl$_2$(2a)]	1 580 (sh)	304m	336m 325 (sh)	7.6—7.3 (m) [30]	7.9—7.7 (m) [2] 6.9—6.4 (m) [6]	3.85 (s) [3] 3.80 (s) [3]	2.27 (s) [3]			
(2d)	1 622ms 1 572ms	198mw		8.6—7.0 (m) [32]	7.0—6.6 (m) [4] 6.3—6.0 (m) [2]	3.85 (s) [3] 3.79 (s) [3]	1.20 (s) [3]			
[CoBr$_2$(2d)]	1 585mw	214mw	275m							
[ZnBr$_2$(2d)]	1 580m	213mw	256ms 248 (sh)	7.7—7.3 (m) [30]	8.0—7.7 (m) [2] 6.9—6.4 (m) [6]	3.90 (s) [3] 3.81 (s) [3]	2.26 (s) [3]			
(2e)	1 639ms 1 620 (sh) 1 572ms	294m or 283m		8.3—7.0 (m) [22]	7.0—6.3 (m) [6]	3.82 (s) [3] 3.28 (s) [3]	1.88 (s) [b]			2.8—1.4 (br m) (PCH$_2$) [b]
[CoCl$_2$(2e)]	1 578m 1 520 (sh)	297m or 285 (sh)	348ms 322ms							
[NiCl$_2$(2e)]	1 575mw 1 530 (sh)	298m or 283mw	343m 330 (sh)							
[CuCl$_2$(2e)]	1 580mw 1 525 (sh)	293m or 285 (sh)	328 (sh) 308m							
[ZnCl$_2$(2e)] [c]	1 580mw 1 523 (sh)	295 (sh) or 283 (sh)	322ms 315ms	8.3—7.3 (m) [22]	7.2—6.5 (m) [6]	3.85 (s) [3] 3.81 (s) [3]	2.40 (s) [b]			2.7—1.5 (br m) (PCH$_2$) [b]
(2b)	1 625s 1 580s	259m		8.3—6.9 (m) [30]			1.37 (s) [d]	4.9—4.2 (br m) [1] 3.2—2.5 (br m) [1]	2.1—0.76 (br m) [d]	
[CoCl$_2$(2b)]·0.25CH$_2$Cl$_2$	1 530ms	297ms	345ms 325m							
[NiCl$_2$(2b)]·0.33CH$_2$Cl$_2$	1 524ms	294m	336ms 307m							
[CuCl$_2$(2b)]·0.25CH$_2$Cl$_2$	1 527ms	291ms or 285 (sh)	320m 291ms or 285 (sh)							
[ZnCl$_2$(2b)]·0.25CH$_2$Cl$_2$ [e]	1 540ms	296ms	326ms 312ms	8.0—7.1 (m)			2.01 [3]		2.2—0.7 (br m)	5.30 (s) (CH$_2$Cl$_2$)
[CoCl$_2$(2c)]	1 530ms	297m	345 (sh) 336ms							
[CuCl$_2$(2c)]	1 536ms	295ms or 286ms	321m 295ms or 286ms							

[a] δ Values are in p.p.m. from SiMe$_4$ as internal standard, in CDCl$_3$ solutions; integration values are given in square brackets, s = singlet, m = multiplet, br = broad. [b] Overlapping signals: integration value = 7. [c] N.m.r. spectrum in CD$_2$Cl$_2$ solution. [d] Overlapping signals: integration value = 23. [e] N.m.r. spectrum in a saturated CDCl$_3$ solution. [f] Not observed.

The ligand (2e) gives adducts [MCl$_2$(2e)] with all the metal chlorides except FeCl$_2$, for which an inseparable mixture of products resulted. The complexes [MCl$_2$(2e)] are all slightly hygroscopic and are less soluble in halogenated solvents than are [MCl$_2$(2a)]. The nickel derivative, [NiCl$_2$(2e)], is so hygroscopic that it must be kept under dry dinitrogen. For this reason its magnetic moment was determined in CH$_2$Cl$_2$ solution rather than in the solid state. This behaviour may be due to reduced protection of the metallic centre M from attack by atmospheric moisture or other reagents, because of the reduced steric hindrance of the chelating diphosphine in (2e) relative to that of the two mutually *trans* PPh$_3$ molecules in (2a). The ligand (2b) easily displaces (2a) from the complex [CoCl$_2$(2a)]. The binuclear complexes [MCl$_2$(2b)] are all sparingly soluble so that molecular weights could not be determined. If they are prepared from dichloromethane solutions, the adducts retain a

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[14] P. Krumholz, O. A. Serra, and M. A. De Paoli, *Inorg. Chim. Acta*, 1975, **15**, 25 and refs. therein.

[15] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, **2**, 173 and refs. therein.

[16] P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.

certain amount of solvent of crystallisation which cannot be completely removed even by heating them *in vacuo* (3—4 h at 60 °C, 10^{-2} mmHg).* The presence of CH_2Cl_2 of crystallisation was confirmed in the case of [$ZnCl_2$-(2b)]·$0.25CH_2Cl_2$ by its ^1H n.m.r. spectrum in $CDCl_3$ (Table 2).

In order to obtain more soluble complexes we replaced the PPh_3 ligands of (2b) by $PMePh_2$. The resulting ligand (2c) was then too soluble to isolate and so its solution was used directly to prepare its transition-metal chloride adducts (see Experimental section).

The binuclear complexes [MX_2(2)] are, in general, monomers in 1,2-dichloroethane solution (Table 1). This fact and the spectroscopic data indicate that complexes (2) act as chelating ligands to the metal centre M, analogously to purely organic α-di-imines.[15,17,18] Only the nickel adducts have molecular weights slightly higher than the calculated values, perhaps because of their partial association through chloride bridges, as was found for complexes of the type [$NiCl_2$(L–L)] (L–L = *NNN'N'*-tetramethylethylenediamines).[19] The magnetic-moment data show that the adducts of Cu^{II}, Ni^{II}, Co^{II}, and Fe^{II} are high-spin paramagnetic complexes (Table 1).

Infrared Spectra.—Typical i.r. bands of the ligands (2) and their adducts are shown in Table 2. The free ligands are characterised by the presence of two C=N stretching vibrations in the range 1 555—1 639 cm^{-1}, which are shifted to lower frequency and markedly reduced in intensity on co-ordination [in most cases only one ν(C=N) band is then observed]. This may be due to the formation of a delocalised π-electron system on the five-membered ring by interaction of the C=N double bonds and d_π orbitals of the central metal M, as was deduced to occur in complexes of organic α-di-imines on the basis of their i.r. and n.m.r. spectra.[20]

In the binuclear complexes formed from (2a) and (2b) the Pd–Cl stretching vibrations are some 30—40 cm^{-1} to higher wavenumbers than those of the free ligands. The bromo-derivatives of the ligand (2d) have Pd–Br bands which are shifted to higher wavenumbers by *ca.* 15 cm^{-1}. This clearly indicates a reduced *trans* influence of the σ-bonded 1,2-bis(arylimino)propyl groups on co-ordination as was also observed when (2a) was protonated.[11] On the other hand, ν(Pd–Cl) of the ligand (2e), in which the chloride is *trans* to a phosphorus atom of the chelating 1,2-bis(diphenylphosphino)ethane ligand (dppe), appears to be little affected by co-ordination, although this band could not be assigned with certainty since two absorptions of comparable intensity occur in the 280—310 cm^{-1} region. {The Pd–Cl band of (2e) is likely to occur in this region because the complex [$PdCl_2$(dppe)] shows two Pd–Cl stretching vibrations at 310 and 286 cm^{-1} respectively.[21]}.

The binuclear complexes show, in general, two M–X stretching bands. The only exception is the complex [$CoBr_2$(2d)], for which only one band was detected at 275 cm^{-1}, probably because of an accidental degeneracy. The $\tilde{\nu}$(M–X) values for the cobalt and zinc adducts are very close to those reported for the tetrahedral (or pseudo-tetrahedral) complexes [MX_2L_2] and [MX_2(L–L)] (M = Co or Zn; X = Cl or Br; L and L–L = various unidentate and chelating bidentate *N*-donor ligands).[22,23] In addition, the values of $\mu_{eff.}$ at room temperature are consistent with those normally found in pseudo-tetrahedral complexes of Co^{II}.[24] Although the position of the M–Cl bands of the $NiCl_2$ and $CuCl_2$ adducts seems to rule out the presence of chloride bridges, some association in the solid through weak long-range metal–halogen interaction may occur, such as is observed, for example, in [CuX_2(2Me-py)$_2$] (2 Me-py = 2-methylpyridine).[25] The $\tilde{\nu}$(Ni–Cl) values, in the range 307—343 cm^{-1}, and the values of $\mu_{eff.}$ at room temperature are similar to those found for other distorted tetrahedral nickel(II) complexes.[22,23,26,27] The position of the ν(Cu–Cl) bands (285—329 cm^{-1}), and $\mu_{eff.}$ (1.80—1.95 B.M.) values of the $CuCl_2$ adducts, do not distinguish between planar or tetrahedral configurations in the solid state. However, we prefer the latter structure, probably with some distortion, on the basis of the electronic spectra of these adducts in solution (see later) and the bulkiness of the ligands (2). In complexes of the type [CuX_2(L–L)] a distorted-tetrahedral configuration is favoured by the steric requirements of the *N*-donor chelating ligand, L–L.[23b,28]

The position of the Fe–Cl stretching vibrations (358 and 327 cm^{-1} respectively) and the value of $\mu_{eff.}$ at room temperature (5.18B.M.) are also consistent with a pseudo-tetrahedral arrangement at iron in the complex [$FeCl_2$(2a)].[23,29] This structure is confirmed by the Mössbauer spectrum at liquid-nitrogen temperature which gives an isomer shift $\delta = 0.96 \pm 0.1$ mm s^{-1} relative to ^{57}Fe and a quadrupole splitting $\Delta E_Q = 2.68$ mm s^{-1}, in the range observed for several tetrahedral iron(II) complexes.[23,29,30]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27×10^{-24} A m^2.

[17] H. Bock and H. tom Dieck, *Chem. Ber.*, 1967, **100**, 228.

[18] H. tom Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 92.

[19] L. Sacconi, I. Bertini, and F. Moni, *Inorg. Chem.*, 1967, **6**, 262.

[20] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963, p. 190; C. Tëuzer, R. Price, E. Breitruaier, G. Jung, and W. Boelter, *Angew. Chem. Internat. Edn.*, 1970, **9**, 963 and refs. therein.

[21] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

[22] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.

[23] (*a*) R. C. Dickinson and G. J. Long, *Inorg. Chem.*, 1974, **13**, 262; (*b*) G. J. Long and D. L. Coffen, *ibid.*, p. 270.

[24] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37; R. L. Carlin, *Transition Metal Chem.*, 1965, **1**, 1.

[25] D. Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chim. Acta*, 1971, **5**, 257; P. Srugh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1657.

[26] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[27] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley–Interscience, New York, 1972, p. 896.

[28] (*a*) I. Bertini and F. Moni, *Inorg. Chem.*, 1967, **6**, 2032; (*b*) A. L. Lott and P. G. Rosmussen, *J. Inorg. Nuclear Chem.*, 1970, **32**, 101.

[29] C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (*A*), 1967, 694; 1968, 1074.

[30] P. R. Edwards, C. E. Johnson, and R. J. P. Williams, *J. Chem. Phys.*, 1967, **47**, 2074.

Hydrogen-1 *N.M.R. Spectra.*—The ^1H n.m.r. spectra of ligands (2) and their corresponding $ZnCl_2$ adducts are reported in Table 2. The spectra of (2a) and its protonated derivative have already been discussed in detail.[11] The spectra of (2d) and (2e) are closely related to that of (2a) since they all contain the same 1,2-bis(*p*-methoxyphenylimino)propyl moiety. The relatively lower-field signal of the methyl group in position 3 (CMe in Table 2) of (2e) is probably due to different shielding effects of the phenyl rings attached to phosphorus in dppe compared to those of the two *trans*-PPh_3 ligands in (2e) and (2d). The ^1H n.m.r. spectrum of (2b) is quite similar to that of its iodo-analogue *trans*-$[PdI\{CNC_6H_{11})CMe(NC_6H_{11})\}(PPh_3)_2]$, obtained by the double insertion of $C_6H_{11}NC$ into the Pd–C σ bond of *trans*-$[PdI(Me)(PPh_3)_2]$.[31]

In all cases, only one of the various possible configurations of the 1,2-bis(arylimino)propyl group is predominant in $CDCl_3$ solution. The signals which are mainly affected by co-ordination to $ZnCl_2$ are those of the phenyl protons of the C_6H_4OMe-*p* substituents and of the CMe group. The C_6H_4OMe-*p* groups of complexes (2a), (2d), and (2e) appear as two non-equivalent AA′BB′ multiplets, one of which is partly masked by the intense PPh resonances of the tertiary phosphine ligands. On co-ordination these masked signals are shifted to lower field (7.7—8.3 p.p.m.) and can be clearly observed.

The assignment of C_6H_4OMe-*p* signals is based on the ^1H n.m.r. spectra of $ZnCl_2$ adducts of analogous derivatives (2) which carry different substituents on the imine nitrogen atoms, such as *trans*-$[PdCl\{C(NR)CMe(NR')\}(PPh_3)_2]$ [$R = C_6H_{11}$, $R' = C_6H_4OMe$-*p*, (3a); $R = C_6H_4OMe$-*p*, $R' =$ Me, (3b)], which will be reported in detail in a later paper.[32] In the case of the complex $[ZnCl_2(3a)]$, the C_6H_4OMe-*p* group in position 2 of the 1,2-bis(arylimino)propyl moiety appears as an AA′BB′ multiplet in the range 6.3—6.9 p.p.m., whereas in $[ZnCl_2(3b)]$ the C_6H_4OMe-*p* group in position 1 appears as two symmtrical signals of a widely spaced AA′BB′ system at 7.6—7.8 and 6.4—6.6 p.p.m. respectively. The C_6H_4OMe-*p* resonances of $[ZnCl_2(2a)]$ result, therefore, from a combination of the spectra of $[ZnCl_2(3a)]$ and $[ZnCl_2(3b)]$. We assign the low-field signal to the *ortho*-protons since they are rather close to the palladium atom and therefore are likely to be deshielded by interaction with the metal, as were the protons of azo- or imino-groups *N*-bonded to Pt^{II}.[33] Such an interaction often leads to *ortho*-metallated products, such as are known for iridium.[34]

The ^1H n.m.r. spectrum of $[ZnCl_2(2a)]$ is very similar to that of (2a) when protonated.[11] It is therefore likely that the 1,2-bis(arylimino)propyl group has the same configuration in both complexes. The signals of the methyl group in position 3 are shifted downfield by 1.06—1.52 p.p.m. on co-ordination. Downfield shifts of 0.22—0.27 p.p.m. also occur on protonation.[11] The larger shifts observed for metallic adducts of derivatives (2) are probably related to a more extensive π-electron delocalisation in the five-membered ring of the binuclear complexes.

Electronic Spectra.—The electronic spectra of the binuclear complexes are reported in Table 3. A typical feature of all these spectra is the presence of a very intense band with a maximum at >25 000 cm^{-1}, but with a tail that in certain cases extends considerably into the visible region of the spectrum. Its position depends on the nature of the co-ordinated metal M and particularly on the *N*-substituents of the ligands (2) suggestive of metal-to-ligand charge-transfer character.[17,18,35]

TABLE 3

Electronic spectra[a]

Complex	Spectral bands (cm^{-1})	
$[FeCl_2(2a)]$		7 020br (54), 5 780 (sh)
$[CoCl_2(2a)]$	16 950 (sh), 15 150 (sh), 14 205 (360)	9 520br (12). 7 350 (67), 6 100br (31)
$[CoBr_2(2d)]$	16 000 (sh), 14 205 (446)	9 430br (12), 6 920 (87), 5 990 (sh)
$[CoCl_2(2e)]$	17 090 (sh), 15 270 (sh), 14 705 (418)	9 615br(19), 7 300 (79), 6 100 (sh)
$[CoCl_2(2b)]\cdot 0.25CH_2Cl_2$	16 805(180), 15 380 (sh), 14 970(448)	9 900br(19), 7 325(86), 6 100br(32)
$[CoCl_2(2c)]$	16 950(157), 15 380 (sh), 14 880(430)	9 900br(14), 7 350(76), 6 130br(32)
$[NiCl_2(2e)]$	*b*	11 495(31), 9 710(48), 8 200 (sh),br
$[NiCl_2(2e)]$	*b*	11 495(36), 9 870(52), 8 330 (sh),br
$[NiCl_2(2b)]\cdot 0.33CH_2Cl_2$	20 000(118), 17 850(sh), 16 130(39)	11 765(43), 10 000(59), 8 250(sh), br
$[CuCl_2(2a)]$	*b*	
$[CuCl_2(2a)]$	*b*	
$[CuCl_2(2b)]\cdot 0.25CH_2Cl_2$		11 110br(104), 7 780br(100)
$[CuCl_2(2c)]$		11 230br(119), 8 000br(108)

[a] Recorded in CH_2Cl_2 solution at room temperature; molar absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses. [b] Masked by the tail of the ligand charge-transfer band (see text).

In the case of ligands (2a), (2d), and (2e) the tail of the charge-transfer band covers a large part of the visible spectrum and is therefore responsible for the orange-brown colour of the complexes. It shifts progressively to lower frequency on passing from cobalt(II) to copper(II) adducts. Thus, for cobalt(II) derivatives a set of *d–d* bands in the range 14 705—17 090 cm^{-1} is still observable, while the corresponding nickel(II)

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[31] Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 1974, **13**, 438.

[32] B. Crociani, M. Nicolini, and R. L. Richards, unpublished work.

[33] J. Kuyper and K. Vrieze, *J. Organometallic Chem.*, 1974, **74**, 289; J. F. Von Bear, K. Vrieze, and D. J. Stufkens, *ibid.*, vol. 81, p. 247.

[34] J. F. Von Bear, K. Vrieze, and D. J. Stufkens, *J. Organometallic Chem.*, 1975, **85**, 249.

[35] H. tom Dieck and I. W. Renk, *Angew. Chem. Internat. Edn.*, 1970, **9**, 793; A. T. T. Hsieh and B. O. West, *J. Organometallic Chem.*, 1974, **78**, C40.

complexes have this region completely masked. For the copper(II) complexes the extension of the tail is such as to hide all the expected *d–d* transitions. In the case of ligands (2b) and (2c) the charge-transfer band shifts to higher frequencies to such an extent that no overlap with *d–d* bands occurs.

The *d–d* transitions of the complex [$FeCl_2$(2a)] consist of a broad absorption at 7 020 cm^{-1} with a shoulder at 5 780 cm^{-1}, a pattern generally observed for pseudo-tetrahedral iron(II) complexes.[23,29,36] Nevertheless, these bands are relatively high which probably indicates a distortion from tetrahedral symmetry.[36,37] In agreement with the conclusions reached from i.r. and magnetic data, the spectra of the cobalt(II), nickel(II), and copper(II) complexes are all consistent with pseudo-tetrahedral geometry,[19,23,28b,38,39] somewhat distorted in the copper case. Probably, the steric bulk of the ligands (2) is important in enforcing tetrahedral geometry on copper.

EXPERIMENTAL

Isocyanides[40] and their palladium complexes, *cis*-[$PdCl_2(CNR)_2$] (R = C_6H_4OMe-*p* or C_6H_{11}),[41] were prepared and purified by published methods. All the other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with Perkin-Elmer 457 (250—4 000 cm^{-1}) and Beckman IR11 (120—400 cm^{-1}) instruments. Hexachlorobutadiene mulls and NaCl plates were used in the range 1 300—4 000 cm^{-1} and Nujol mulls and CsI plates or thin Polythene discs in the range 120—1 700 cm^{-1}. Electronic spectra in CH_2Cl_2 solution were recorded with a Cary model 14 recording spectrophotometer in the range 5 000—25 000 cm^{-1} at room temperature, using quartz cells of 1- or 5-cm path length. Hydrogen-1 n.m.r. spectra were obtained with Varian NV-14 60 MHz or JEOL PS100 instruments at room temperature using $SiMe_4$ as internal reference. Magnetic moments were determined in the solid state with a Bruker Magnet BM6 instrument or with a recording Faraday balance at 22 °C. Magnetic moments in CH_2Cl_2 solution were measured by published methods.[42] Molecular weights were determined with a Mechrolab osmometer at 37 °C in 1,2-dichloroethane. The Mössbauer spectrum was recorded at 80 K by a constant-acceleration spectrometer using a ^{57}Co-in-Pt matrix source at room temperature. The velocity scale was calibrated with 99.99% ^{57}Fe foil. (We thank Dr. S. Calogero for this measurement.) Elemental analyses were by A. Berton and G. Biasioli of the Microanalytical Laboratory, Laboratorio Radioelementi C.N.R., Padova.

Preparations.—trans-[PdX{C(NR)CMeNR)}L_2]. (*i*) (2a; X = Cl, R = C_6H_4OMe-*p*, L = PPh_3). The complex *cis*-[$PdCl_2(CNC_6H_4OMe$-*p*$)_2$] (2.24 g, 5 mmol) was suspended in benzene (150 cm^3) and treated with a benzene solution of $HgMe_2$ (12.5 cm^3 of a 0.615 mol dm^{-3} solution, 7.5 mmol). The resulting mixture was stirred for 7—8 h, then treated with PPh_3 (2.62 g, 10 mmol). On addition of the tertiary phosphine the solid material quickly dissolved and the colour changed from yellow-green to dark red. The reaction was complete in *ca.* 15 min as shown by i.r. spectroscopy of the solution (see text). The resulting solution was treated with charcoal, filtered, then concentrated to 5—6 cm^3 under reduced pressure. Addition of diethyl ether gave a yellow precipitate which was filtered off, washed with ether, and dried *in vacuo*. The remaining HgMeCl was removed by sublimation (80—100 °C, 10^{-2} mmHg, 3 h). The yellow *product* was further purified by reprecipitation from CH_2Cl_2 with diethyl ether (yield 75—80%).

Complexes (2b) and (2c) were similarly prepared (reaction time, 90 min). The yield of (2b) was 50% (reprecipitated from diethyl ether–hexane), but (2c) was so soluble that it was prepared in benzene solution and used in subsequent reactions without prior isolation.

(*ii*) (2d; X = Br, R = C_6H_4OMe-*p*, L = PPh_3). Complex (2a) (0.95 g, 1 mmol) was dissolved in CH_2Cl_2–acetone (1 : 1 v/v) and treated with NaBr (0.68 g). The reaction mixture was stirred for 18 h then taken to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (80 cm^3) and the solution treated with charcoal, then filtered. The resulting solution was concentrated to small volume and the yellow *product* precipitated by addition of diethyl ether. It was purified by reprecipitation from the same solvents (yield 72%).

cis-[1,2-*Bis*(*diphenylphosphino*)*ethane*]*chloro*[1,2-*bis*(p-*methoxyphenyl*)*iminopropyl*]*palladium*, (2e). Complex (2a) (1.42 g, 1.5 mmol) was dissolved in CH_2Cl_2 (100 cm^3) and treated with 1,2-bis(diphenylphosphino)ethane (0.72 g, 1.8 mmol). After 4 h the solution was treated with charcoal, filtered, and concentrated to small volume under reduced pressure. Addition of diethyl ether then gave the yellow *product* which was purified by reprecipitation from the same solvents (yield 76%).

Chloro{2,2-*dichloro*-5-*methyl*-1,3-*bis*(p-*methoxyphenyl*)-2-*ferra*-1,3-*diazol*-4-*yl*}*bis*(*triphenylphosphine*)*palladium*, [$FeCl_2$(2a)]. Anhydrous $FeCl_2$ (0.110 g) and iron filings (0.110 g) under dinitrogen were suspended in anhydrous CH_2Cl_2 (80 cm^3) and treated with the complex (2a) (0.475 g, 0.5 mmol). The reaction mixture was vigorously stirred overnight, treated with charcoal, then filtered to give a clear red solution which was concentrated to small volume. Addition of anhydrous di-ethyl ether gave a yellow precipitate which turned red-brown when dried *in vacuo*. This *product* (0.45 g) was purified by reprecipitation from the same solvents.

[MCl_2(2a)], [MBr_2(2d)], *and* [MCl_2(2e)] (M = Co, Ni, Cu, *or* Zn). All these binuclear complexes were prepared by the same general method and so only the preparation of [MCl_2(2a)] is described. Anhydrous MCl_2 (0.5 mmol) was dissolved in absolute ethanol (5—10 cm^3) (in the case of $NiCl_2$ some heating was necessary) and treated dropwise with a solution of the ligand (2a) (0.5 mmol) in CH_2Cl_2 (30 cm^3). An immediate change of colour to red or red-brown occurred. After 1 h the reaction mixture was treated with charcoal, filtered, and evaporated at reduced pressure

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[36] W. A. Baker, jun., and P. M. Lutz, *Inorg. Chim. Acta*, 1976, **16**, 5.

[37] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 454.

[38] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690; D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4**, 139; A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.* (*A*), 1966, 859; E. R. Menzel, W. R. Vincent, D. K. Johnson, G. L. Seebach, and J. R. Wasson, *Inorg. Chem.*, 1974, **13**, 2465.

[39] D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 1963, 207; E. Uhlig, J. Csarzar, and M. Maarez, *Z. anorg. Chem.*, 1964, **331**, 324.

[40] I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem. Internat. Edn.*, 1965, **4**, 472.

[41] B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.

[42] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

until the product began to precipitate. Precipitation was completed by the addition of diethyl ether. The binuclear *complexes* were purified by successive precipitations from CH_2Cl_2 solutions with either diethyl ether or diethyl ether–ethanol (3 : 1 v/v). The yields were 80—90% for [MCl_2-(2a)] and [MBr_2(2d)] and 75—80% for [MCl_2(2e)]. No well characterised product could be obtained from the reaction of $CuBr_2$ with (2d) or from the reaction of $FeCl_2$ with (2e).

[MCl_2(2b)]·$n$$CH_2Cl_2$ (M = Co, Cu, *or* Zn, n = 0.25; M = Ni, n = 0.33). The ligand (2b) (0.5 mmol) dissolved in benzene (80 cm^3) was added dropwise to a stirred solution of anhydrous MCl_2 (0.5 mmol) in absolute ethanol (4—10 cm^3). After stirring for 30 min the reaction mixture was taken to dryness, the solid residue was dissolved in CH_2Cl_2 (250 cm^3), and the solution treated with charcoal then filtered. The resulting clear solution was slowly concentrated to small volume at reduced pressure whereupon a partial precipitation of the product occurred, which was completed by addition of diethyl ether. The *products* were purified by reprecipitation from the same solvents (yields 60—70%).

[MCl_2(2c)] (M = Co *or* Cu). The anhydrous MCl_2 compounds (1 mmol) dissolved in absolute ethanol (20 cm^3) were treated dropwise with a benzene solution of (2c) obtained from the preparation of this derivative as described above. After stirring for 30 min the reaction mixture was taken to dryness and the solid residue extracted with benzene (100 cm^3). The resulting solution was treated with charcoal, filtered, concentrated to small volume, and the *product* precipitated by addition of diethyl ether. Analytically pure samples were obtained after two successive precipitations from the same solvents (yields 50—60% based on MCl_2).

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