Journal of Organometallic Chemistry, 479 (1994) 37–46

Reactivity of tetranuclear cyclometallated palladium(II) halide-bridged complexes of bis(*N*-benzylidene)-1,4-phenylenediamines

José M. Vila, Miguel Gayoso, Teresa Pereira, Camino Rodríguez, Juan M. Ortigueira, Jesús J. Fernández and M. López Torres

Department of Inorganic Chemistry, University of Santiago, Santiago de Compostela, E-15706 (Spain)

(Received July 29, 1993)

Abstract

Treatment of the cyclometallated halide-bridged complexes [{1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)}$_2$C$_6$H$_4$}$_2$] (**Ia**, **IIa**) and [{1,4-{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(X)}$_2$C$_6$H$_4$}$_2$] (**Ib**, **IIb**) (X = Cl or Br) with ditertiary diphosphines in a complex/diphosphine 1:2 molar ratio gave the 26- and 28-membered ring tetranuclear cyclometallated complexes [1,4-{{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)}$_2$C$_6$H$_4$}$_2${μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$] (**1a**: X = Cl, n = 3; **2a**: X = Br, n = 3; **3a**: X = Cl, n = 4; **4a**: X = Br, n = 4) and [1,4-{{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N](X)}$_2$C$_6$H$_4$}$_2${μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$}$_2$] (**1b**: X = Cl, n = 3; **2b**: X = Br, n = 3; **3b**: X = Cl, n = 4; **4b**: X = Br, n = 4) and in a complex/diphosphine 1:4 molar ratio gave the dinuclear cyclometallated complexes [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N]}$_2$C$_6$H$_4${Ph$_2$P(CH$_2$)$_n$PPh$_2$-*P*,*P*}$_2$][PF$_6$]$_2$ (**5a**: n = 3; **6a**: n = 4) and [1,4-{Pd[2,4-(MeO)$_2$C$_6$HC(H)=N]}$_2$C$_6$H$_4$}{Ph$_2$P(CH$_2$)$_n$PPh$_2$-*P*,*P*}$_2$][PF$_6$]$_2$ (**5b**: n = 3; **6b**: n = 4).

Treatment of the cyclometallated halide-bridged complexes [{1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)}$_2$C$_6$H$_4$}$_2$] (**Ia**, **IIa**) and [{1,4-{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N](X)}$_2$C$_6$H$_4$}$_2$] (**Ic**, **IIc**) (X = Cl, Br) with tertiary monophosphines in a complex/phosphine 1:4 or 1:8 molar ratio gave the new dinuclear cyclometallated complexes [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)(L)}$_2$C$_6$H$_4$] [L = PPh$_3$: **7a** (X = Cl), **8a** (X = Br); L = PPhEt$_2$: **9a** (X = Cl), **10a** (X = Br); L = PPh(C≡CPh)$_2$: **11a** (X = Cl), **12a** (X = Br)] and [1,4-{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N](X)(L)}$_2$C$_6$H$_4$] [L = PPh$_3$: **1c** (X = Cl), **2c** (X = Br); L = PPhEt$_2$: **3c** (X = Cl), **4c** (X = Br); L = PPh(C≡CPh)$_2$: **5c** (X = Cl), **6c** (X = Br)] and non-cyclometallated complexes [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)(L)$_2$}$_2$C$_6$H$_4$] [L = PPh$_3$: **13a** (X = Cl), **14a** (X = Br); L = PPhEt$_2$: **15a** (X = Cl), **16a** (X = Br); L = PPh(C≡CPh)$_2$: **17a** (X = Cl), **18a** (X = Br)] and [1,4-{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N](X)(L)$_2$}$_2$C$_6$H$_4$] [L = PPh$_3$: **7c** (X = Cl), **8c** (X = Br); L = PPhEt$_2$: **9c** (X = Cl), **10c** (X = Br); L = PPh(C≡CPh)$_2$: **11c** (X = Cl), **12c** (X = Br)], respectively. Reaction of the halide-bridged complexes with thallium acetylacetonate gave the dinuclear cyclometallated complexes [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](H$_3$CCOCHCOCH$_3$)}$_2$C$_6$H$_4$] (**19a**) and [1,4-{Pd[4,5-(OCH$_2$O)C$_6$H$_2$C(H)=N](H$_3$CCOCHCOCH$_3$)}$_2$C$_6$H$_4$] (**13c**). The compounds were characterized by microanalysis (C, H, N), IR and ^{31}P{^{1}H} and ^{1}H spectroscopy.

Key words: Palladium; Nuclear magnetic resonance; Polynuclear; Infrared spectroscopy; Cyclometallation; Halide-bridged complexes

1. Introduction

The chemistry of cyclometallated compounds is very extensive and has been covered in general reviews [1–4]. The use of cyclometallated compounds of transition metals in regiospecific organic synthesis is now well known [5–7]. We have investigated cyclometallated compounds containing different types of nitrogen ligand such as Schiff bases [8–10], phenylimidazoles donor [11], benzylidene hydrazones [12], diimines derived from terephthalaldehydes [13] and bis(*N*-benzylidene)-1,4-phenylenediamines [14], as well as some of their reactions with, for example, tertiary monophosphines and ditertiary diphosphines. In the case of the complexes with bis(*N*-benzylidene)-1,4-phenylenediamines, non-polymeric tetranuclear halide-bridged compounds were obtained [14] as opposed to related complexes of polymeric nature [15–17]. These tetranuclear compounds react with a wide range of molecular and anionic nucleophiles to give new tetranuclear and dinuclear species. Recently, we have reported their reac-

---

Correspondence to: Dr. J.M. Vila.

0022-328X/94/$7.00
SSDI 0022-328X(94)24443-M

tions with ditertiary diphosphines to give cyclometallated tetranuclear complexes with large rings (up to 28-membered ring species); the study of such compounds overlaps with the now growing field of supramolecular chemistry [18]. In the present paper we describe the synthesis and characterization of compounds derived from the tetranuclear halide-bridged complexes by reaction of the latter with ditertiary diphosphines to give 26- and 28-membered ring cyclometallated palladium(II) complexes and with tertiary monophosphines or thallium acetylacetonate to give dinuclear cyclometallated and non-cyclometallated palladium(II) complexes.

2. Results and discussion

We have previously described the preparation and characterization of the tetranuclear halide-bridged precursors (**Ia**, **IIa**, **Ib**, **IIb**, **Ic**, **IIc**) used in the synthesis of the complexes in the present paper [14].

2.1. *Reactions with ditertiary diphosphines*

Treatment of an acetone suspension of the tetranuclear halide-bridged compounds **Ia**, **IIa**, **Ib** and **IIb** with the ditertiary diphosphines $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) in a 1:2 halide-bridged complex/diphosphine molar ratio afforded the tetra-

TABLE 1. Microanalytical, colour, yield and IR data [a] of prepared complexes

Complex	Colour	Yield (%)	Analytical data: found (calcd.) (%)			IR data (cm^{-1})		
			C	H	N	ν(C=N) [b]	ν(Pd–Cl)	ν(C≡C)
1a	Yellow	72	54.8 (54.8)	4.5 (4.8)	2.2 (2.4)	1602 (sh, m)	289 (m)	
2a	Yellow	66	50.7 (50.9)	4.6 (4.4)	1.9 (2.2)	1604 (sh, m)		
3a	Yellow	75	55.1 (55.2)	4.9 (4.9)	2.4 (2.4)	1603 (sh, m)	292 (m)	
4a	Yellow	86	51.5 (51.3)	4.7 (4.5)	2.2 (2.2)	1605 (sh, m)		
5a	Yellow	67	54.1 (53.7)	4.2 (4.4)	1.9 (1.6)	1604 (sh, m)		
6a	Orange	82	54.2 (54.2)	4.1 (4.5)	1.7 (1.5)	1607 (sh, m)		
7a	Yellow	78	59.1 (58.6)	4.4 (4.4)	2.3 (2.2)	1603 (m)	305 (m)	
8a	Yellow	81	55.3 (55.0)	4.2 (4.0)	2.0 (2.1)	1605 (m)		
9a	Yellow	75	51.4 (51.3)	5.1 (5.2)	2.5 (2.6)	1604 (m)	300 (m)	
10a	Yellow	69	47.4 (47.4)	4.6 (4.8)	2.4 (2.4)	1600 (m)		
11a	Yellow	61	61.5 (61.6)	3.8 (4.0)	2.1 (2.1)	1601 (m)	308 (m)	2186 (s)
12a	Yellow	68	57.8 (57.8)	3.7 (3.7)	1.9 (2.0)	1602 (m)		2181 (s)
13a	Yellow	83	65.5 (65.6)	5.1 (4.8)	1.6 (1.6)	1606 (m)	298 (m)	
14a	Yellow	80	62.1 (62.5)	4.5 (4.6)	1.5 (1.5)	1603 (m)		
15a	Yellow	72	56.2 (56.3)	5.8 (5.9)	2.0 (2.0)	1606 (m)	292 (m)	
16a	Yellow	74	53.0 (53.0)	5.4 (5.5)	1.9 (1.9)	1605 (m)		
17a	Pale yellow	65	68.5 (69.0)	4.4 (4.2)	1.4 (1.4)	1610 (sh)	305 (m)	2185 (s)
18a	Pale yellow	67	65.6 (65.9)	4.2 (4.0)	1.4 (1.4)	1612 (m)		2180 (s)
19a	Yellow	75	49.1 (49.3)	4.4 (5.1)	2.9 (3.2)	1604 (m)		
1b	Yellow	59	55.9 (55.7)	4.6 (4.5)	2.5 (2.5)	1597 (sh, m)	280 (w)	
2b	Yellow	81	51.3 (51.5)	4.0 (4.1)	2.6 (2.4)	1598 (sh, m)		
3b	Orange	70	55.9 (56.1)	4.3 (4.5)	2.5 (2.5)	1594 (sh, m)	299 (w)	
4b	Orange	74	52.3 (52.0)	4.1 (4.3)	2.2 (2.3)	1597 (sh, m)		
5b	Orange	69	46.8 (47.0)	4.6 (4.4)	1.6 (1.6)	1603 (m)		
6b	Orange	61	47.2 (47.6)	4.8 (4.5)	1.7 (1.5)	1604 (m)		
1c	Yellow	79	59.0 (59.1)	3.7 (3.7)	2.3 (2.4)	1610 (m)	310 (m–w)	
2c	Yellow	82	55.1 (53.6)	3.2 (3.5)	2.2 (2.2)	1612 (m)		
3c	Yellow	74	53.5 (53.6)	4.4 (4.5)	2.7 (2.8)	1605 (m)	310 (m)	
4c	Yellow	71	48.9 (49.1)	3.9 (4.1)	2.4 (2.6)	1600 (m)		
5c	Yellow	65	62.1 (62.2)	3.2 (3.5)	2.1 (2.2)	1604 (m)	289 (m)	2169 (s)
6c	Yellow	68	58.3 (58.1)	3.0 (3.2)	2.1 (2.1)	1600 (m)		2164 (s)
7c	Yellow	85	66.2 (66.3)	4.5 (4.4)	1.7 (1.6)	1620 (m)	302 (m)	
8c	Yellow	80	62.9 (63.0)	4.2 (4.2)	1.6 (1.6)	1618 (m)		
9c	Yellow	76	59.2 (59.3)	5.9 (5.9)	2.0 (2.2)	1615 (m)	304 (m)	
10c	Yellow	77	55.4 (55.3)	5.2 (5.5)	2.0 (2.1)	1617 (m)		
11c	Pale yellow	61	69.4 (69.7)	3.9 (3.9)	1.5 (1.5)	1610 (m)	280 (m–w)	2178 (s)
12c	Pale yellow	63	66.2 (66.6)	3.8 (3.8)	1.5 (1.4)	1605 (m)		2163 (s)
13c	Yellow	71	49.0 (49.1)	3.5 (3.9)	3.4 (3.6)	1610 (sh)		

[a] s, strong; m, medium; w, weak; sh, shoulder. [b] ν(C=N) values (in cm^{-1}) for: **a**, 1612 (m); **b**, 1615 (m); **c**, 1630 (m).

nuclear cyclometallated complexes $[1,4\text{-}\{\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)\text{=}N](X)\}_2C_6H_4\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2]$ (**1a**: X = Cl, *n* = 3; **2a**: X = Br, *n* = 3; **3a**: X = Cl, *n* = 4; **4a**: X = Br, *n* = 4) and $[1,4\text{-}\{\{Pd[2,4\text{-}(MeO)_2C_6H_2\text{-}C(H)\text{=}N](X)\}_2C_6H_4\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2]$ (**1b**: X = Cl, *n* = 3, **2b**: X = Br, *n* = 3; **3b**: X = Cl, *n* = 4; **4b**: X = Br, *n* = 4). The compounds were obtained as air-stable yellow solids, which have been fully characterized by elemental analysis (C, H, N), IR and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (see Tables 1 and 2). The dinuclear cyclometallated moieties are linked by two ditertiary diphosphines, dppp or dppb, to give 26- and

TABLE 2. $^{31}P\{^1H\}$ [a] and ^1H [b] NMR data [c,d] of prepared complexes

Complex	δ(HC=N)	δ[H(6)]	δ[H(5)]	δ(MeO)	δ(OCH$_2$O)	δ(C$_6$H$_4$)	δ(P)
a [e]	8.79 (s)	7.92 (d) ^3J[H(5)H(6)] = 8.8	6.81 (d)	3.91 (s) 3.94 (s) 3.99 (s)		7.27 (s)	
1a	8.50 (d) ^4J(PH) = 6.8		5.80 (d) ^4J[PH(5)] = 6.1	2.93 (s) 3.71 (s) 3.95 (s)		7.32 (s)	32.74 (s)
2a	8.49 (d) ^4J(PH) = 6.5		5.80 (d) ^4J[PH(5)] = 6.0	2.94 (s) 3.71 (s) 3.95 (s)		7.32 (s)	33.01 (s)
3a	8.47 (d) ^4J(PH) = 7.0		5.80 (d) ^4J[PH(5)] = 6.4	2.90 (s) 3.73 (s) 3.97 (s)		7.49 (s)	33.70 (s)
4a	8.50 (d) ^4J(PH) = 7.0		5.78 (d) ^4J[PH(5)] = 6.5	2.89 (s) 3.72 (s) 3.94 (s)		7.50 (s)	33.59 (s)
5a	8.12 (d) ^4J(PH) = 7.0		5.90 (dd) ^4J[P$_a$H(5)] = 7.6 ^4J[P$_b$H(5)] = 7.8	2.96 (s) 3.76 (s) 4.10 (s)		6.25 (s)	24.01 (d, P$_a$) − 4.37 (d, P$_b$) ^3J(PP) = 52.0
6a	8.23 (d) ^4J(PH) = 7.7		5.97 (dd) ^4J[P$_a$H(5)] = 6.0 ^4J[P$_b$H(5)] = 9.1	2.92 (s) 3.79 (s) 4.17 (s)		6.57 (s)	30.14 (d, P$_a$) 16.20 (d, P$_b$) ^4J(PP) = 17.0
7a	8.46 (d) ^4J(PH) = 7.1		5.77 (d) ^4J[PH(5)] = 6.1	2.83 (s) 3.71 (s) 3.93 (s)		7.30	41.64 (s)
8a	8.50 (d) ^4J(PH) = 7.1		5.77 (d) ^4J[PH(5)] = 6.6	2.86 (s) 3.71 (s) 3.93 (s)		7.31 (s)	41.46 (s)
9a	8.51 (d) ^4J(PH) = 6.9		5.79 (d) ^4J[PH(5)] = 6.3	3.09 (s) 3.73 (s) 3.93 (s)		7.41 (s)	36.79 (s)
10a	8.53 (d) ^4J(PH) = 6.9		5.79 (d) ^4J[PH(5)] = 6.4	3.11 (s) 3.74 (s) 3.94 (s)		7.39 (s)	35.16 (s)
11a	8.52 (d) ^4J(PH) = 7.4		6.76 (d) ^4J[PH(5)] = 8.9	3.44 (s) 3.77 (s) 3.98 (s)		7.35 (s)	−20.27 (s)
12a	8.54 (d) ^4J(PH) = 7.6		6.75 (d) ^4J[PH(5)] = 9.1	3.44 (s) 3.79 (s) 3.90 (s)		7.35 (s)	−20.82 (s)
13a	8.34 (s)		6.00 (s)	2.98 (s) 3.70 (s) 3.80 (s)		7.30 (s)	27.05 (s)
14a	8.25 (s)		6.23 (s)	3.13 (s) 3.68 (s) 3.69 (s)		7.31 (s)	27.03 (s)
15a	8.52 (s)		6.05 (s)	3.37 (s) 3.75 (s) 3.80 (s)		7.36 (s)	10.41 (s)
16a	8.58 (s)		6.13 (s)	3.45 (s) 3.75 (s) 3.79 (s)		7.36 (s)	9.11 (s)

28-membered ring species, respectively, which may be regarded as macrocyclic cyclometallated complexes (see Scheme 1). There are, in principle, other possible geometries for the disposition of the diphosphine ligands in the complexes; however, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy proved to be invaluable tools for distinguishing the structures. Thus, the ^1H NMR spectra show only one set of signals for each type of hydrogen nucleus (see Table 2). The doublet at δ *ca.* 8.50 ppm (**1a–4a**, **1b–4b**) is assigned to the *H*C=N resonance, which is shifted to lower frequency with respect to the corresponding free donor [19,20]. The doublet at δ *ca.*

TABLE 2 (continued)

Complex	δ(HC=N)	δ[H(6)]	δ[H(5)]	δ(MeO)	δ(OCH$_2$O)	δ(C$_6$H$_4$)	δ(P)
17a	8.52 (s)		6.77 (s)	3.44 (s) 3.76 (s) 3.98 (s)		7.35 (s)	−25.29 (s)
18a	8.53 (s)		6.76 (s)	3.45 (s) 3.77 (s) 3.98 (s)		7.35	−27.88 (s)
19a [f]	8.27 (s)		6.92 (s)	3.81 (s) 3.98 (s) 4.00 (s)		7.45 (s)	

Complex	δ(HC=N)	δ[H(3)]	δ[H(5)]	δ(MeO)	δ(OCH$_2$O)	δ(C$_6$H$_4$)	δ(P)
b [e]	8.83 (s)	6.47 (dd) ^3J[H(3)H(5)] = 2.3	6.70 (dd)	3.86 (s) 3.87 (s)		7.25 (s)	
1b	8.56 (d) ^4J(PH) = 7.0	5.95 (d) ^3J[H(3)H(5)] = 2.0 ^4J[PH(5)] = 6.1	5.65 (dd)	2.98 (s) 3.74 (s)		7.29 (s)	32.42 (s)
2b	8.56 (d) ^4J(PH) = 7.1	5.95 (d) ^3J[H(3)H(5) = 2.0 ^4J[PH(5)] = 6.0	5.66 (dd)	2.98 (s) 3.74 (s)		7.29 (s)	34.14 (s)
3b	8.53 (d) ^4J(PH) = 7.4	5.94 (d) ^3J[H(3)H(5)] = 1.7 ^4J[PH(5)] = 6.0	5.65 (dd)	2.95 (s) 3.72 (s)			33.08 (s)
4b	8.46 (d) ^4J(PH) = 7.7	5.96 (d) ^3J[H(3)H(5)] = 1.6 ^4J[PH(5)] = 6.1	5.69 (dd)	2.97 (s) 3.74 (s)			33.14 (s)
5b	8.16 (d) ^4J(PH) = 7.3	6.06 (d) ^3J[H(3)H(5)] = 2.0 ^4J[P$_a$H(5)] = 6.7 ^4J[P$_b$H(5)] = 9.0	5.79 (ddd)	3.12 (s) 3.88 (s)		6.23 (s)	13.16 (d, P$_a$) 9.51 (d, P$_b$) ^3J(PP) = 38.1
6b	8.26 (d) ^4J(PH) = 6.8	6.10 (d) ^3J[H(3)H(5)] = 1.9 ^4J[P$_a$H(5)] = 6.9 ^4J[P$_b$H(5)] = 8.9	5.83 (ddd)	3.07 (s) 3.92 (s)		6.50 (s)	28.07 (d, P$_a$) 17.12 (d, P$_b$) ^4J(PP) = 18.3

Complex	δ(HC=N)	δ[H(2)]	δ[H(3)]	δ(MeO)	δ(OCH$_2$O)	δ(C$_6$H$_4$)	δ(P)
c [e]	8.40 (s)	7.30 (dd) ^3J[H(2)H(3)] = 7.9	6.90 (d)		6.05 (s)		7.25 (s)
1c	n.a.	6.69 (d) ^3J[H(2)H(3)] = 8.0	6.03 (d)		5.25 (s)	7.23 (s)	36.37 (s)
2c	n.a.	6.67 (d) ^3J[H(2)H(3)] = 8.0	6.02 (d)		5.29 (s)	7.23 (s)	36.56 (s)
3c	8.20 (d) ^4J(PH) = 6.4	7.09 (d) ^3J[H(2)H(3)] = 7.8	6.48 (d)		4.92 (s)	7.39 (s)	31.29 (s)
4c	8.22 (d) ^4J(PH) = 6.4	7.09 (d) ^3J[H(2)H(3)] = 7.8	6.48 (d)		4.92 (s)	7.35 (s)	32.23 (s)
5c	7.39 (d) ^4J(PH) = 7.3	7.13 (d) ^3J[H(2)H(3)] = 7.8	6.57 (d)		5.42 (s)	7.27 (s)	−27.46 (s)
6c	7.39 (d) ^4J(PH) = 8.1	7.11 (d) ^3J[H(2)H(3)] = 7.8	6.57 (d)		5.45 (s)	7.28 (s)	−28.81 (s)

TABLE 2 (continued)

Complex	δ(HC=N)	δ[H(2)]	δ[H(3)]	δ(MeO)	δ(OCH_2O)	δ(C_6H_4)	δ(P)
7c	8.62 (s)	6.79 (d) ^3J[H(2)H(3)] = 8.0	6.06 (d)		5.13 (s)	7.24 (s)	20.71 (s)
8c	8.75 (s)	6.78 (d) ^3J[H(2)H(3)] = 8.0	6.08 (d)		5.14 (s)	7.25 (s)	20.22 (s)
9c	8.54 (s)	7.44 (d) ^3J[H(2)H(3)] = 8.0	6.51 (d)		5.65 (s)	6.82 (s)	11.33 (s)
10c	8.57 (s)	7.49 (d) ^3J[H(2)H(3)] = 8.7	6.54 (d)		5.72 (s)	6.84 (s)	10.29 (s)
11c	8.29 (s)	7.12 (d) ^3J[H(2)H(3)] = 7.9	6.55 (d)		5.43 (s)	7.32 (s)	−31.86 (s)
12c	8.24 (s)	7.08 (d) ^3J[H(2)H(3)] = 7.9	6.52 (d)		5.49 (s)	7.30 (s)	−37.34 (s)
13c [f]	7.95 (s)	7.09 (d) ^3J[H(2)H(3)] = 7.8	6.03 (d)		6.06 (s)	7.37 (s)	

[a] Spectra measured at 100.6 MHz (*ca.* ±20°C); chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. [b] Spectra measured at 250 MHz (*ca* ±20°C); chemical shifts(δ) in ppm (±0.01) to high frequency of $SiMe_4$. [c] Coupling constants in Hz. [d] s, singlet; d, doublet; dd, doublet of doublets; n.a., not assigned, occluded by the phosphine resonances. [e] δ[H(6)]: **b**, 7.13 (d, ^3J[H(5)H(6)] = 8.6 Hz); **c**, 7.20 (d, ^4J[H(2)H(6)] = 1.4 Hz). [f] acac: **a**, δ(Me) 2.08 (s), 1.90 (s); δ(CH) 5.36 (s). **c**, δ(Me) 2.09 (s), 1.86 (s); δ(CH) 5.39 (s).

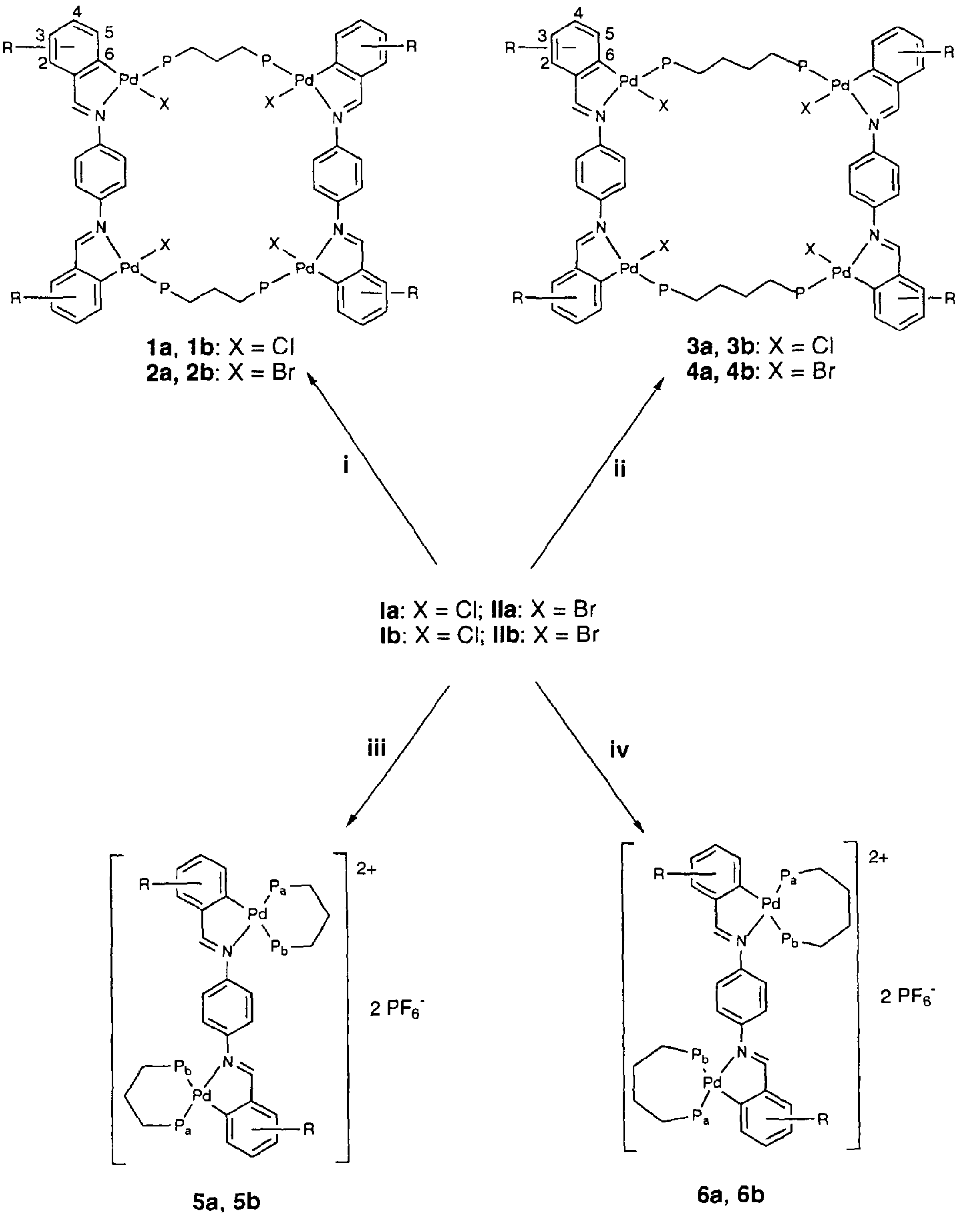
5.80 ppm (**1a–4a**) and the doublet of doublets at δ *ca.* 5.60 ppm (**1b–4b**) are assigned to the *H*(5) resonances which are coupled to the ^{31}P nucleus. The singlet at δ *ca.* 2.95 ppm is assigned to the C(4)-*Me*O resonance, which is shifted by approximately 1 ppm to lower frequency with respect to the free donor [21]. The other proton resonances have been assigned as in Table 2.

The $^{31}P\{^1H\}$ NMR spectra all show only one singlet. The chemical shifts are consistent with the phosphorus atoms being *trans* to the nitrogen atom [13]. These NMR results are in accord with the geometry depicted in Scheme 1 for **1a–4a** and **1b–4b**, where the diphosphines are on the 'outer' side of the [Pd(X)(μ-PP)Pd(X)] moiety. With one of the phosphines on the 'inner' side, with both phosphorus atoms *trans* to the carbon atoms, a more complex $^{31}P\{^1H\}$ NMR spectra would be expected, *e.g.* the phosphorus nuclei *trans* to nitrogen and *trans* to carbon would have different chemical shifts, and in a *trans*-C–Pd–P geometry the *H*C=N resonance would not be coupled to the ^{31}P nucleus [8] (see below). In a sterically hindered geometry with both diphosphines *trans* to carbon atoms, the chemical shifts in both the $^{31}P\{^1H\}$ and ^1H NMR spectra, as well as the coupling constants, would be quite different from those observed for the present complexes. Furthermore, higher frequencies of ν(Pd–X) would be expected in the IR spectra. Another possible structure for the complexes is polymeric, but mass spectroscopic determinations show the complexes to be tetranuclear. Analogous complexes with smaller 'bite' ditertiary diphosphines are presently under study [22].

Reaction of the tetranuclear halide-bridged compounds **Ia**, **IIa**, **Ib** and **IIb** with the ditertiary diphosphines $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) in a 1:4 halide-bridged complex/diphosphine molar ratio in the presence of NH_4PF_6 afforded the dinuclear cyclometallated complexes $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](X)\}_2C_6H_4\{Ph_2P(CH_2)_nPPh_2P,P\}_2][PF_6]_2$ (**5a**: $n = 3$; **6a**: $n = 4$;) and $[1,4\text{-}\{Pd[2,4\text{-}(MeO)_2C_6H_2C(H)=N](X)\}_2C_6H_4\{Ph_2P(CH_2)_nPPh_2P,P\}_2][PF_6]_2$ (**5b**: $n = 3$; **6b**: $n = 4$). The final products were the same whichever halide starting material was used, as the halogen was replaced by the hexafluorophosphate ion; the molar conductivities in dry acetonitrile showed they are 1:2 electrolytes. The ^{31}P NMR spectrum showed two doublets for the two inequivalent phosphorus nuclei. The assignment of the doublets to each phosphorus nucleus was made on the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus nucleus *trans* to it to lower frequency [23]. This was confirmed by selective decoupling experiments on the P_a and P_b atoms. The *H*C=N resonance (doublet) is coupled to only one phosphorus nucleus [^4J(PH) = *ca.* 7.5 Hz] presumably that *trans* to it. Selective irradiation of the P_a or P_b resonances reduced the *H*(5) resonance to a doublet [^4J(PH) = *ca.* 7.5 Hz] and the *H*C=N resonance to a singlet (irradiating at P_a), whereas the latter remain unchanged upon irradiating P_b.

2.2. Reactions with tertiary monophosphines

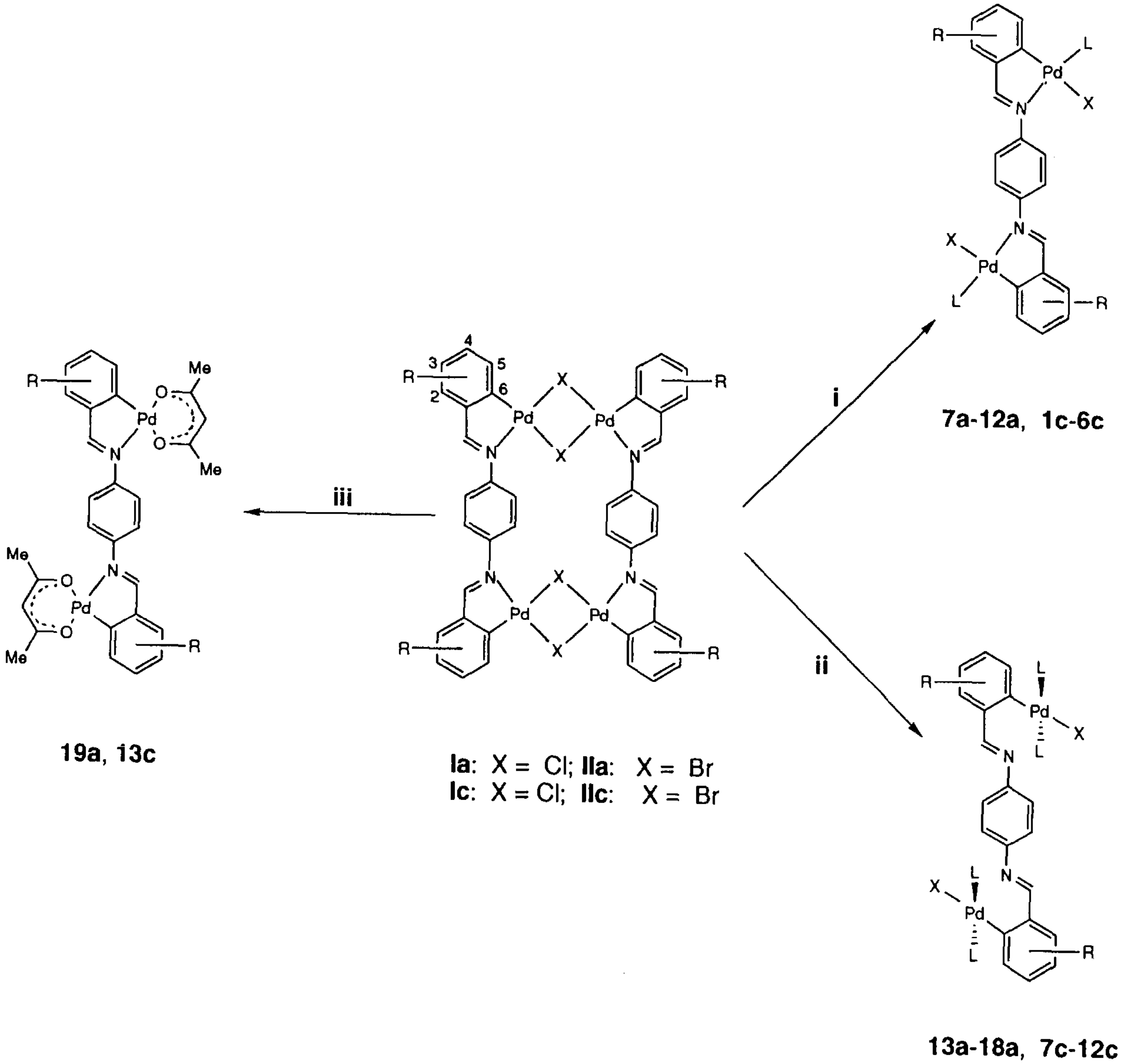
Treatment of an acetone suspension of the tetranuclear halide-bridged compounds **Ia**, **IIa**, **Ic** and **IIc** with the tertiary monophosphines triphenylphosphine, diethylphenylphosphine and bis(phenylacetylide)phenyl-phosphine in 1:4 or 1:8 halide-bridged complex/phosphine molar ratios gave the dinuclear cyclometallated [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N](X)(L)}$_2$C$_6$H$_4$] [L = PPh$_3$: **7a** (X = Cl), **8a** (X = Br); L = PPhEt$_2$: **9a** (X = Cl), **10a** (X = Br); L = PPh(C≡CPh)$_2$: **11a** (X = Cl), **12a** (X = Br)] and [1,4-{Pd[4,5-(OCH$_2$O)C$_6$H$_2$-C(H)=N](X)(L)}$_2$C$_6$H$_4$] [L = PPh$_3$: **1c** (X = Cl), **2c** (X = Br); L = PPhEt$_2$: **3c** (X = Cl), **4c** (X = Br); L = PPh(C≡CPh)$_2$: **5c** (X = Cl), **6c** (X = Br)] and non-cyclometallated [1,4-{Pd[2,3,4-(MeO)$_3$C$_6$HC(H)=N]-



Scheme 1. i: 2 equiv. of Ph$_2$P(CH$_2$)$_3$PPh$_2$ in acetone; ii: 2 equiv. of Ph$_2$P(CH$_2$)$_4$PPh$_2$ in acetone; iii: 4 equiv. of Ph$_2$P(CH$_2$)$_3$PPh$_2$ in acetone; iv: 4 equiv. of Ph$_2$P(CH$_2$)$_4$PPh$_2$ in acetone. **a**: R = 2,3,4-(MeO)$_3$C$_6$H; **b**: R = 2,4-(MeO)$_2$C$_6$H$_2$.

$(X)(L)_2\}_2C_6H_4]$ [L = PPh_3: **13a** (X = Cl), **14a** (X = Br); L = $PPhEt_2$: **15a** (X = Cl), **16a** (X = Br); L = $PPh(C{\equiv}CPh)_2$: **17a** (X = Cl), **18a** (X = Br)] and [1,4-$\{Pd[4,5\text{-}(OCH_2O)C_6H_2C(H){=}N](X)(L)_2\}_2C_6H_4$] [L = PPh_3: **7c** (X = Cl), **8c** (X = Br); L = $PPhEt_2$: **9c** (X = Cl), **10c** (X = Br); L = $PPh(C{\equiv}CPh)_2$: **11c** (X = Cl), **12c** (X = Br)] complexes, respectively. The reactions of **Ia**, **IIa**, **Ic** and **IIc** with the phosphines is summarized in Scheme 2. The dinuclear complexes are air-stable yellow or pale yellow solids, readily soluble in organic solvents such as chloroform, dichloromethane, acetone, methanol and diethyl ether.

All the complexes have been fully characterized by elemental analysis (C, H, N), IR and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (see Tables 1 and 2). The $^{31}P\{^1H\}$ NMR spectra of compounds **7a–12a** and of **1c–6c** show only one singlet with chemical shifts consistent with phosphines *trans* to the nitrogen atom [13]. This is confirmed by the ^1H NMR spectra which show only one set of resonances for each type of proton. The results suggest that the complexes adopt the symmetrical conformation shown in Scheme 2. The *H*C=N proton resonances (**7a–12a**, **3c–6c**) show long-range coupling to phosphorus with $^4J[PH]$ = *ca.* 6.5–7.0 Hz for L = PPh_3 or $PPhEt_2$, and slightly larger *ca.* 7.4–8.0 Hz for L = $PPh(C{\equiv}CPh)_2$ (see Table 2). The *H*(5) proton resonance (**7a–12a**) is also coupled to phosphorus in every case, with $^4J[PH]$ = *ca.* 6.0–6.5 Hz for L = PPh_3, $PPhEt_2$; for L = $PPh(C{\equiv}CPh)_2$ larger values are obtained for $^4J[PH]$, *i.e.* *ca.* 9.0 Hz. Irradiation of the ^{31}P



Scheme 2. i: 4 equiv. of PR_3 in acetone; ii: 8 equiv. of PR_3 in acetone; iii: 4 equiv. of Tl(acac) in dichloromethane. a: R = 2,3,4-$(MeO)_3C_6H$; c: R = 4,5-$(OCH_2O)C_6H_2$. See text for identity of PR_3.

resonance caused the HC=N and H(5) doublet resonances to collapse to singlets. The HC=N resonance is shifted to lower frequency relative to that of the free donor and this is consistent with coordination of the palladium atom to the C=N moiety through the nitrogen atom [19,20]; this is confirmed by the shift of the ν(C=N) frequency towards lower wavenumbers in the IR spectra [19] (see Table 1).

Complexes **13a–18a** and **7c–12c** are non-electrolytes in dry acetonitrile ($< 7\ \Omega^{-1}$ cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solutions at 20°C). With Schiff bases and two phosphine ligands displacing two halogen atoms [8] 1 : 2 electrolytes are formed. This is consistent with the ν(Pd–Cl) stretch at *ca.* 300 cm^{-1} (see Table 1). Furthermore, in these complexes the second phosphine ligand breaks the Pd–N bond. The PdL$_2$X moiety can rotate about the Pd–C vector so that the palladium coordination plane is at 90° to the metallated phenyl ring, eliminating coupling between the ^{31}P atom and the H(5) or the HC=N protons in complexes **13a–18a** [8] so that these proton resonances are singlets (see Table 2).

Only one singlet is observed in the ^{31}P{^{1}H} NMR spectra of compounds **13a–18a** and **7c–12c** (see Scheme 2). This, together with the chemical shifts, is consistent with a *trans* arrangement of the phosphines [24] as confirmed by the very weak band at *ca.* 550 cm^{-1} in the IR spectra [25]. The phosphorus resonance in the non-cyclometallated complexes (phosphorus *trans* to phosphorus) is shifted to lower frequency compared to the corresponding cyclometallated compounds (phosphorus *trans* to nitrogen) (see Table 2) due to the different *trans* influences of the ligands *trans* to the ^{31}P nuclei [26].

In the other possible symmetrical conformation depicted in Fig. 1, the close approach of the palladium and hydrogen atoms would give rise to a large paramagnetic shift (> 1 ppm) of the HC=N resonance, which was not observed [27]. Another feature of the non-cyclometallated complexes is that in some cases such as **13a**, **14a**, **11c** and **12c** where there is apparently no Pd–N bond (see above), the HC=N resonance is shifted strongly to lower frequency compared to that of the parent free base. The values for ν(C=N) are also smaller than expected. We have observed this before [8] and the structures suggest that some Pd ··· N interaction may be present in these complexes [15,28].

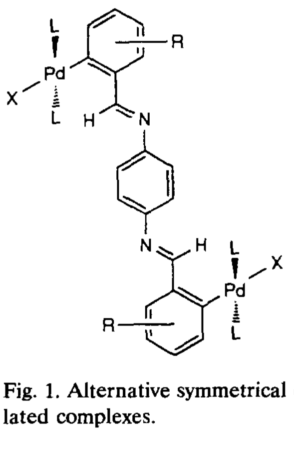


Fig. 1. Alternative symmetrical conformation for the non-cyclometallated complexes.

There is a shift to lower frequency of one MeO resonance, C(4)-MeO, in **7a–12a** by δ *ca.* 1 ppm (L = PPh$_3$), *ca.* 0.8 ppm (L = PPhEt$_2$) and *ca.* 0.5 ppm [L = PPh(C≡CPh)$_2$]. This is due to the shielding effects of the phosphine phenyl rings, showing that the phosphine is *trans* to the nitrogen atom [21]. When L = PPh(C≡CPh)$_2$, the larger distance of the phenyl ring (C≡CPh) from the phosphorus nucleus means it is further from the MeO group and therefore exerts a smaller influence on the shift of the MeO resonance. The third phenyl ring (P–Ph) is probably not at the correct angle to influence the MeO group, in contrast to the case in PPhEt$_2$. In complexes **13a–18a** the C(4)-MeO resonance is also shifted to lower frequency by the phosphines, now *trans* (see Table 2).

A similar trend is found in complexes **1c–6c**, where the OCH_2O resonance is also shifted to lower frequency due to an analogous shielding effect. For complexes **7c–12c** a similar shift of the OCH_2O resonance is observed, with smaller shifts for **9c** and **10c**, *i.e.* only δ 0.40 (**9c**) and δ 0.33 (**10c**) ppm (*cf.* **3c** and **4c** with shifts of *ca.* 1.1 ppm) (see Table 2).

The singlet resonance of H(5) is shifted to lower frequency by *ca.* 1 ppm in complexes **7a–10a** and by *ca.* 0.5–0.8 ppm in complexes **13a–16a**. However, in complexes **11a**, **12a** and **17a**, **18a** this shift is negligible (see Table 2). Although it has been argued that the shift of this proton resonance could be due to electron flow from the electron-rich metal to the phenyl ring upon metallation [29], we believe these results clearly show it is associated with the shielding effects of a phosphine phenyl ring (once again bringing the phosphine ligand *trans* to the nitrogen atom in complexes **7a–12a**). In complexes with L = PPh(C≡CPh)$_2$, the phosphine has almost no effect on the H(5) resonance for the reasons given above. In complex **19a**, where there is no phosphine, the H(5) shift is practically unchanged, and in the tetranuclear halide-bridged complexes the chemical shift values δ[H(5)] are 6.70 (s) ppm (**Ia**) and 6.86 (s) ppm (**IIa**) [14].

The ^{31}P chemical shifts are in the order δ(PPh$_3$) > δ(PPhEt$_2$) > δ(PPh(C≡CPh)$_2$) for both cyclometallated and non-cyclometallated complexes. We have previously observed such trends in phosphorus resonances [8].

2.3. Reactions with thallium acetylacetonate

Treatment of a dichloromethane suspension of the tetranuclear halide-bridged complexes with thallium acetylacetonate gave the dinuclear cyclometallated complexes $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](H_3CCOCHCOCH_3)\}_2C_6H_4]$ (**19a**) and $[1,4\text{-}\{Pd[4,5\text{-}(OCH_2O)C_6H_2C(H)=N](H_3CCOCHCOCH_3)\}_2C_6H_4]$ (**13c**). The same products were obtained regardless of the halogen atom in the starting material (**Ia**, **Ic** or **IIa**, **IIc**). The readily soluble dinuclear species **19a** and **13c** are air-stable solids which were fully characterized by elemental analysis (C, H and N), and IR and ^1H NMR spectroscopy (see Tables 1 and 2, and Scheme 2). These derivatives also have the symmetrical conformation shown in Scheme 2. The IR spectra show C–C and C–O stretches in the expected ranges. The ^1H NMR spectra show two sets of methyl resonances, with singlets at δ 2.08 and 1.90 ppm (**19a**) and δ 2.05 and 1.95 ppm (**13c**), which can be assigned to the acetylacetonate methyl groups. The assignments of the remaining proton resonances are also included in Table 2.

3. Experimental details

Solvents were purified by standard methods [30]. Chemicals were reagent grade. Elemental analyses were carried out with a Carlo Erba elemental analyzer, model 1108. IR spectra were recorded as Nujol mulls or polythene discs with a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$) using a Bruker WM-250 spectrometer. We described earlier the synthesis of the halide-bridged tetranuclear complexes (**Ia**, **IIa**, **Ic**, **IIc**) [14].

3.1. Preparation of $[\{1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](Cl)\}_2C_6H_4\}_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}_2]$ (1a)

To a suspension of **Ia** (0.050 g, 0.034 mmol) in acetone (*ca.* 15 cm^3), $Ph_2P(CH_2)_3PPh_2$ (0.028 g, 0.068 mmol) was added. The mixture was stirred for 12 h at room temperature and filtered. The resulting solution was concentrated under reduced pressure and chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol(15%) afforded the final product as a yellow powder after concentration. Recrystallization was effected from chloroform/hexane. Compounds **2a**–**4a** and **1b**–**4b** were prepared in a similar manner.

3.2. Preparation of $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N]\}_2C_6H_4\{Ph_2P(CH_2)_3PPh_2\text{-}P,P\}_2][PF_6]_2$ (5a)

To a suspension of **Ia** (0.040 g, 0.027 mmol) in acetone (*ca.* 15 cm^3), $Ph_2P(CH_2)_3PPh_2$ (0.045 g, 0.108 mmol) was added. The mixture was stirred for 6 h at room temperature, after which ammonium hexafluorophosphate was added and the mixture was stirred for another 6 h and filtered. The resulting solution was concentrated under reduced pressure and chromatographed on silica gel. Elution with dichloromethane/ethanol(4%) afforded the desired product as a yellow solid after concentration. Recrystallization was effected from chloroform/hexane. Compounds **5b**, **6a** and **6b** were prepared similarly.

3.3. Preparation of $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](Cl)(PPh_3)\}_2C_6H_4]$ (7a)

To a suspension of **Ia** (0.031 g, 0.021 mmol) in acetone (*ca.* 5 cm^3), PPh_3 (0.022 g, 0.084 mmol) was added. The mixture was stirred for 2 h at room temperature and the resulting precipitate was filtered off and dried *in vacuo*. Recrystallization from chloroform/hexane gave the desired product as a yellow solid. Complexes **8a**–**12a** and **1c**–**6c** were prepared similarly.

3.4. Preparation of $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](Cl)(PPh_3)_2\}_2C_6H_4]$ (13a)

The complex was synthesized in a similar manner to **1a** but using a 1:8 **Ia**/PPh_3 molar ratio (0.026 g, 0.017 mmol and 0.036 g, 0.136 mmol, respectively). Recrystallization from chloroform/hexane gave the desired product as a yellow solid. Complexes **14a**–**18a** and **7c**–**12c** were prepared similarly.

3.5. Preparation of $[1,4\text{-}\{Pd[2,3,4\text{-}(MeO)_3C_6HC(H)=N](H_3CCOCHCOCH_3)\}_2C_6H_4]$ (19a)

To a suspension of **Ia** in dichloromethane, thallium acetylacetonate (0.037 g, 0.122 mmol) was added and the mixture stirred at room temperature for 1 h. The resulting solution was chromatographed on silica gel. Elution with dichloromethane/chloroform (3:1) afforded the desired complex, which was recrystallized from dichloromethane/hexane to give a yellow solid. Complex **13c** was prepared similarly.

Acknowledgements

We wish to thank the Ministerio de Educacion y Ciencia (DGICYT, Proyecto No. PS90-0198) for support and the Xunta de Galicia for grants to J.M.O. and to J.J.F.

References

1 I. Omae, *Coord. Chem. Rev.*, *53* (1984) 261.

2 I. Omae, *Organometallic Intramolecular-coordination Compounds*, Elsevier Science Publishers, Amsterdam/New York, 1986.

3 V.V. Dunina, O.A. Zalevskaya and V.M. Potapov, *Russ. Chem. Rev.*, *571* (1988) 250.

4 A.D. Ryabov, *Chem. Rev.*, *90* (1990) 403.

5 G.R. Newkome, W.E. Puckett, W.K. Gupta and G.E. Kiefer, *Chem. Rev.*, *86* (1986) 451.

6 A. Albinati, P.S. Pregosin and P. Ruedi, *Helv. Chim. Acta*, *68* (1985) 2046.

7 A.D. Ryabov, *Synthesis*, *3* (1985) 233.

8 J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernandez and M. Thornton-Pett, *J. Organomet. Chem.*, *401* (1991) 385.

9 J.M. Vila, M. Gayoso, M.T. Pereira, J.M. Ortigueira, A. Fernandez, H. Adams and N.A. Bailey, *Polyhedron*, *12* (1993) 171.

10 J.M. Vila, M. Gayoso, A. Fernandez, H. Adams and N.A. Bailey, *J. Organomet. Chem.*, *448* (1993) 233.

11 A. Suarez, J.M. Vila, M.T. Pereira, E. Gayoso and M. Gayoso, *J. Organomet. Chem.*, *335* (1987) 359.

12 J.L. Casas, E. Gayoso, J.M. Vila, M.T. Pereira and M. Gayoso, *Synth. React. Inorg. Met.-Org. Chem.*, *21* (1991) 263.

13 J.M. Vila, M. Gayoso, M.T. Pereira, M. Lopez Torres, G. Alonso and J.J. Fernandez, *J. Organomet. Chem.*, *445* (1993) 287.

14 (a) **Ia**, **IIa**, **Ic**, **IIc**: J.M. Vila, M. Gayoso, M.T. Pereira, M.C. Rodriguez, J.M. Ortigueira and M. Thornton-Pett, *J. Organomet. Chem.*, *426* (1992) 267; (b) **Ib**, **IIb**: J.M. Ortigueira, *Ph.D. Dissertation*, Santiago de Compostela, 1993.

15 J. Granell, J. Sales, J. Vilarrasa, J.P. Declerq, G. Germain, C. Miravitlles and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1983) 2441.

16 R.M. Ceder and J. Sales, *J. Organomet. Chem.*, *294* (1985) 389.

17 R.M. Ceder, J. Sales, X. Solans and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, (1986) 1351.

18 J.M. Vila, M. Gayoso, J.M. Ortigueira, M.T. Pereira and M. Lopez Torres, *29th Int. Conf. Coord. Chem.*, Lausanne, Switzerland, July (1992), 19–23, Abs. P 300.

19 H. Onoue and I. Moritani, *J. Organomet. Chem.*, *43* (1972) 431.

20 Y.A. Ustinyuk, V.A. Chertov and J.V. Barinov, *J. Organomet. Chem.*, *29* (1971) C53.

21 J.M. Vila, A. Suarez, M.T. Pereira, E. Gayoso and M. Gayoso, *Polyhedron*, *6* (1987) 1003.

22 J.M. Vila, M. Gayoso and J.M. Ortigueira, unpublished results.

23 J.M. Vila, M. Gayoso J.J. Fernandez, J.M. Ortigueira and A. Suarez, *Polyhedron*, *22* (1990) 2741.

24 M.T. Pereira, J.M. Vila, A. Suarez, E. Gayoso and M. Gayoso, *Gazz. Chim. Ital.*, *118* (1988) 783.

25 S. Mastin, *Inorg. Chem.*, *13* (1974) 2250.

26 P.S. Pregosin and R.W. Kuntz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, in P. Diehl, E. Fluck and R. Kosfeld (eds.), *NMR 16*, Springer, Berlin, 1979.

27 R.G. Miller, R.D. Stauffer, D.R. Fahey and D.R. Parnell, *J. Am. Chem. Soc.*, *92* (1970) 1511.

28 J. Granell, D. Sainz, J. Sales and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1986) 1785.

29 M.A. Gutierrez, G.R. Newkome and J. Selbin, *J. Organomet. Chem.*, *202* (1980) 341.

30 D.D. Perrin, W.L.F. Armarego and D.P. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon Press, Oxford, 1983.