Synthesis and Characterization of Bis(diphenylphosphino)-methanide and -amide Complexes of Ni^{II} and Pd^{II}. Crystal Structure of $[PdCl(Ph_2PNPPh_2)(PEt_3)]$†

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The reaction of $Li[Ph_2PYPPh_2]$ (Y = CH or N) with $[MX_2L_2]$ (M = Ni or Pd; X = Cl or Br; L = PPh_3, PMe_2Ph or PEt_3) has been studied. With Y = CH only palladium derivatives $[PdCl(Ph_2PCHPPh_2)L]$ were obtained; subsequent reaction with Grignard reagents, MgBr(R), gave $[PdR(Ph_2PCHPPh_2)L]$ (R = mesityl or *o*-tolyl). With Y = N, nickel and palladium complexes, $[MX(Ph_2PNPPh_2)(PEt_3)]$, were obtained only with PEt_3. The compounds $[Pd(Ph_2PNPPh_2)_2]$ or $[\{Ni(\mu\text{-}Cl)(Ph_2PNPPh_2)\}_2]$ were formed using PPh_3 or PMe_2Ph instead of PEt_3. Treatment of these complexes with HBF_4 yielded the corresponding cationic complexes containing the neutral chelate ligand. These complexes have been characterized by IR, ^1H and ^{31}P NMR spectroscopy. The complex $[PdCl(Ph_2PNPPh_2)(PEt_3)]$ crystallizes in the monoclinic space group *C2/c*, with a = 18.416(6), b = 11.702(4), c = 27.620(9) Å, β = 93.50(4)° and Z = 8. The P–N bond distances 1.64–1.65 Å are consistent with delocalization of the negative charge in the anionic ligand. The P ··· P distance, 2.440 Å, is close to a single P–P bond length.

In the last few years it has been found that late transition-metal complexes containing chelate ligands are good precursors in homogeneous catalysis. One of the most important processes, the SHOP process,[1] achieves linear oligomerization of ethylene by nickel complexes containing P–O ligands [P–O = $Ph_2PZC(R')O^-$; Z = CH, N, CMe or COH; R' = Ph, OEt or $CHMe_2$]. These anionic ligands function as four-electron donor ligands and lead to five-membered metallacycles. More recently, analogous complexes containing P–N [amino(bis)iminophosphorane][2] and P–P (phosphaalkene)[3] ligands giving four-membered complexes have been described. Although they are less active than the P–O derivatives, the formation of linear polyethylene from ethylene has been reported.

In order to extend the type of potentially catalytic active compounds for oligomerization and polymerization of olefins, we have prepared new nickel and palladium complexes of the type [MX(PYP)L] (X = halide, mesityl or *o*-tolyl; L = PPh_3, PEt_3 or PMe_2Ph) containing the anionic ligands bis(diphenylphosphino)methanide, $Ph_2PCHPPh_2$, or bis(diphenylphosphino)amide, Ph_2PNPPh_2, derived from $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PNHPPh_2$ (dppa) respectively. As chelates, these ligands are four-electron donor systems forming four-membered metallacycles. Although the catalytic activity expected for palladium compounds is not very high, they can facilitate the structural characterization of the complexes.

The compound dppm has been widely studied as a neutral ligand owing to its ability to give different modes of coordination.[4] However, few complexes with the anionic chelate ligand $Ph_2PCHPPh_2$ have been reported so far. The only nickel and palladium derivatives described are $[M(Ph_2PCHPPh_2)\{(CH_2)_2PEt_2\}]$ (M = Ni or Pd)[5] and $[Pd(C_6F_5)(Ph_2PCHPPh_2)(PR_3)]$ (R_3 = Ph_3, Ph_2Et or Ph_2Me).[6] Nakamura and co-workers[7] reported that the reaction of bis(β-diketonato)palladium(II) with dppm gives the homoleptic derivative $[Pd(Ph_2PCHPPh_2)_2]$. The only complexes of Ni and Pd containing the Ph_2PNPPh_2 ligand reported so far are $[M(Ph_2PNPPh_2)_2]$ (M = Pd or Pt) and $[\{Ni(\mu\text{-}Cl)(Ph_2PNPPh_2)\}_2]$.[8]

Results and Discussion

The general method used in the preparation of the new complexes consists in the reaction of the lithium salts $Li[Ph_2PYPPh_2]$ (Y = CH or N), which were prepared *in situ* from the neutral ligand, with metallic complexes. With $[PdCl_2L_2]$ the complexes $[PdCl(Ph_2PCHPPh_2)L]$ **1** (L = PPh_3 **a**, PMe_2Ph **b** or PEt_3 **c**) were obtained in good yields (≈70%). However, from the organopalladium complexes $[PdBr(R)L_2]$ (R = mesityl or *o*-tolyl) the corresponding $[PdR(Ph_2PCHPPh_2)L]$ **2** (R = mesityl, L = PPh_3 **a** or PMe_2Ph **b**) and **3** (R = *o*-tolyl, L = PPh_3 **a** or PMe_2Ph **b**) were obtained in low yield (≈30%). Probably the size of the organic ligand, which is more bulky than the halide, hinders substitution of the phosphine ligand L by the anionic chelate group. Compounds **2** and **3** can be obtained in higher yields by reaction of **1** with Grignard reagents, or from the cationic species $[PdBr(R)(PPh_3)_2]^+$ and the lithium reagent (Scheme 1).

The analogous methanidenickel derivatives could not be obtained, even with very electronegative groups such as C_2Cl_3 which stabilize organonickel compounds.[9] Thus, no reaction was observed when $Li[Ph_2PCHPPh_2]$ was added to the nickel complexes $[NiX_2L_2]$ (X = Cl or Br, L = PPh_3, PMe_2Ph or PEt_3), and it was not possible to characterize any compound from the action of the lithium salt on $[NiX_2L_2]$ or $[Ni(thf)RL_2]^+$ (R = mesityl or C_2Cl_3).

Nickel and palladium derivatives of Ph_2PNPPh_2 have been obtained (Scheme 2). The compounds $[MX(Ph_2PNPPh_2)(PEt_3)]$ (M = Pd, X = Cl **4c**; M = Ni, X = Br **5c**) were obtained by reaction of $[MX_2(PEt_3)_2]$ with the lithium reagent $Li[Ph_2PNPPh_2]$ which was prepared *in situ* by reaction of the amine with $LiBu^n$ at low temperature, in the presence of free phosphine PEt_3, in order to prevent the formation of $[Pd(Ph_2PNPPh_2)_2]$ or $[\{Ni(\mu\text{-}Cl)(Ph_2PNPPh_2)\}_2]$. For other monodentate phosphines studied, L = PPh_3 and PMe_2Ph, the final product was the homoleptic compound [Pd-

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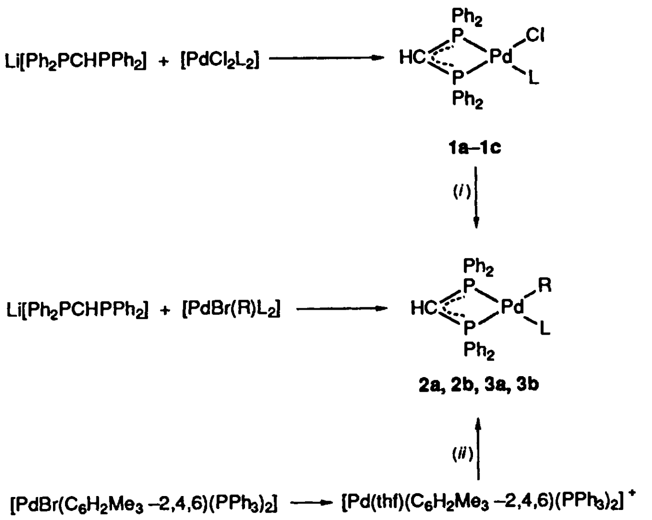
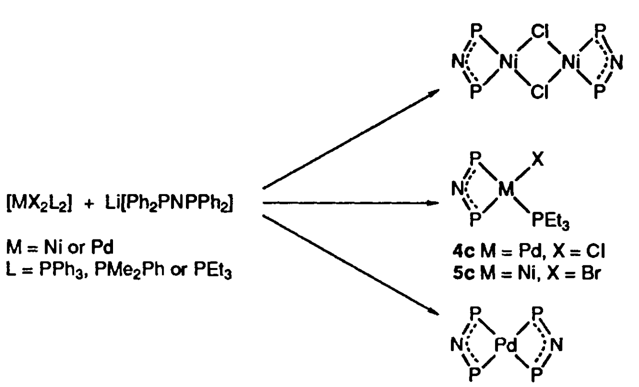
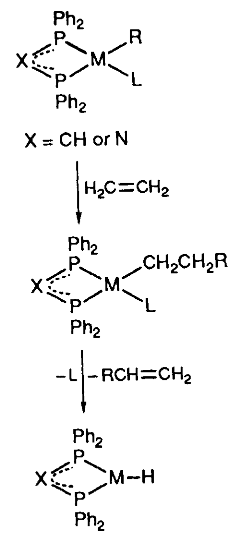
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 thf = Tetrahydrofuran; L = PPh_3 **a**, PMe_2Ph **b** or PEt_3 **c**. (*i*) MgBr(R), R = mesityl **2** or *o*-tolyl **3**; (*ii*) $Li[Ph_2PCHPPh_2]$



Scheme 2



Scheme 3

$(Ph_2PNPPh_2)_2]$ for palladium, and the dinuclear one, $[\{Ni(\mu\text{-}Cl)(Ph_2PNPPh_2)\}_2]$, for nickel. This dinuclear complex reacts only with PEt_3 giving the compound **5c**; no reaction was observed with the other phosphines (PMe_2Ph, PPh_3).

In order to obtain cationic derivatives, $AgClO_4$ was added to $[PdCl(Ph_2PNPPh_2)(PEt_3)]$ but a complex mixture was formed. It was possible to characterize, but not to isolate, one heterometallic compound with the silver co-ordinated to the nitrogen atom and the homoleptic complex $[Ag(Ph_2PNPPh_2)_2]$.[10b] To confirm the NMR assignment, this homoleptic silver complex was obtained by reaction of $Li[Ph_2PNPPh_2]$ and $AgBF_4$ (see Experimental section).

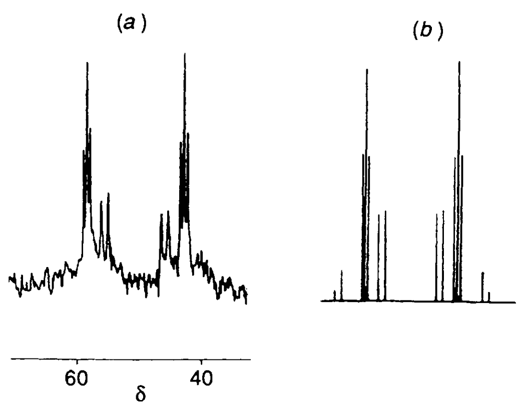


Fig. 1 Proton NMR spectra of the complex $[\{Ag(\mu\text{-}Ph_2PNPPh_2)\}_2]$: (*a*) experimental, at 32.4 MHz (CD_2Cl_2, 220 K); (*b*) simulated spectra of the three isotopomers (see text)

The action of HBF_4 on the new compounds results in protonation of the ligand and formation of the corresponding cationic complexes $[MX(dppa)(PEt_3)]^+$ (M = Pd, X = Cl **6c** or M = Ni, X = Br **7c**). This process is reversible, and the addition of $LiBu^n$, leads to the starting compound.

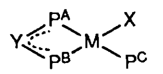
The catalytic activity of the compounds has been tested in the oligomerization of ethylene at 40 bar (4 x 10^6 Pa) and 95 °C, using toluene as solvent. The organometallic compounds **2** and **3** were used solely as precursors, because the insertion of ethylene and subsequent β elimination produces the hydrido-complex which is the catalytic active species (Scheme 3). For the halogeno complexes **1**, **4** and **5**, $AlEt_3$ was added ($Ni:AlEt_3$ = 1:2) in order to promote the formation of the hydrido-complex. With the complex $[NiBr(Ph_2PNPPh_2)(PEt_3)]$ and $AlEt_3$ (as cocatalyst) only, low quantities of but-1-ene (C_4:Ni = 90:1) and traces of hex-1-ene were detected.

Characterization.—All new compounds obtained are air-stable solids, but in solution they decompose slowly under nitrogen. Their IR spectra show the bands typical of co-ordinated monophosphines and the organic ligands R. Cationic complexes **6c** and **7c** exhibit a strong broad band at ≈1060 cm^{-1} due to the anion BF_4^-.[11] Two strong absorptions in the range 800–950 cm^{-1} characteristic of the P–Y–P (Y = CH or N) skeleton are observed.[10]

The ^1H and ^{31}P NMR chemical shifts and the *J*(P–P) values of the compounds are given in Table 1. The ^{31}P spectra belong to the ABC spin system, containing three non-equivalent nuclei; all assignments have been verified using computer simulation with the PANIC program.[12] The $\delta(^{31}P)$ values of the anionic chelate ligands are at higher fields than those for the non-metallated phosphines (δ −22.4 for dppm, and 43.3 for dppa), in accord with the size effect for four-membered metallacycles.[13] In contrast to what is observed for the analogous compounds $[M(C_6F_5)(Ph_2PCHPPh_2)(PR_3)]^6$ (M = Pd or Pt), the P^A atoms, *trans* to the monodentate phosphine ligand, show higher negative $\delta(^{31}P)$ than do the P^B atoms, *trans* to the X or R ligand.

In order to confirm the assignment of the ^{31}P NMR spectra of the Ph_2PNPPh_2 derivatives, the compound $[\{Ag(\mu\text{-}Ph_2PNPPh_2)\}_2]$[10b] has been studied. Its spectrum is the sum of those of the three isotopomers: ^{107}Ag–^{107}Ag, ^{109}Ag–^{109}Ag and ^{107}Ag–^{109}Ag, with relative percentages of 25, 25 and 50%. This complex shows a spin system of the AA′XX′ type, the experimental and simulated spectra being shown in Fig. 1. The chemical shift is δ 53.8 and the coupling constants $^1J(P\text{–}^{107}Ag)$ = 465.5 and $^1J(P\text{–}^{109}Ag)$ = 537.1 Hz, meanwhile the three-bond coupling constants are 18.9 and 19.9 Hz, respectively. The values of the coupling constants indicate the relative

Table 1 Proton and $^{31}P-\{^1H\}$ NMR data[a]



M = Ni or Pd
Y = CH or N; $P^A = P^B = PPh_2$
$P^C = PPh_3, PMe_2Ph$ or PEt_3
X = halide or organic ligand

Compound	$\delta(^{31}P)$			$^2J(P-P)$			$\delta(^1H)$
	P^A (dd)[b]	P^B (dd)	P^C (dd)	A–B	A–C	B–C	CH (dt)
4c $[PdCl(Ph_2PNPPh_2)(PEt_3)]$	−42.8	−18.9	13.9	153.8	450.2	21.2	—
5c $[NiBr(Ph_2PNPPh_2)(PEt_3)]$	−34.2[c]	11.6	−1.0	270.0	270.0	34.6	—
1c $[PdCl(Ph_2PCHPPh_2)(PEt_3)]$	−56.4	−41.1	13.0	75.0	420.4	8.2	2.7
1b $[PdCl(Ph_2PCHPPh_2)(PMe_2Ph)]$	−58.3	−42.0	−8.0	71.6	439.0	4.7	2.3
1a $[PdCl(Ph_2PCHPPh_2)(PPh_3)]$	−56.9	−44.9	19.4	73.2	415.0	5.0	2.1
2a $[Pd(C_6H_2Me_3\text{-}2,4,6)(Ph_2PCHPPh_2)(PPh_3)]$	−41.9	−34.3	20.7	21.3	371.0	18.0	2.4
3a $[Pd(C_6H_4Me\text{-}o)(Ph_2PCHPPh_2)(PPh_3)]$	−59.5	−47.6	18.5	65.1	424.7	—[d]	2.4
2b $[Pd(C_6H_2Me_3\text{-}2,4,6)(Ph_2PCHPPh_2)(PMe_2Ph)]$	−59.4	−44.3	−9.4	71.0	444.0	5.6	—[d]
3b $[Pd(C_6H_4Me\text{-}o)(Ph_2PCHPPh_2)(PMe_2Ph)]$	−59.0	−44.0	10.0	72.0	445.0	—[d]	—[d]

[a] δ in ppm and *J* in Hz. *T* = 220 K. Solvents: Ph_2PNPPh_2 derivatives in CH_2Cl_2, dppm derivatives in toluene. [b] dd = Doublet of doublets, dt = doublet of triplets. [c] Triplet. [d] Not observed.

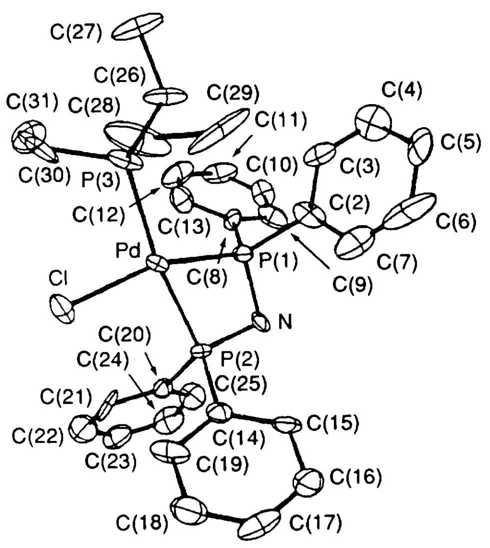


Fig. 2 Molecular structure of complex **4c**

Table 2 Final atomic coordinates (× 10^4) for complex **4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	−4 543(2)	57 485(3)	−13 247(1)
P(1)	−5 090(6)	74 529(10)	−9 560(4)
P(2)	−16 026(5)	63 600(10)	−11 913(4)
P(3)	7 896(7)	54 329(14)	−14 498(5)
Cl	−7 786(7)	40 223(10)	−17 391(5)
N	−1 400(2)	7 632(3)	−969(2)
C(2)	−125(3)	8 698(5)	−1 237(2)
C(3)	574(3)	9 091(6)	−1 086(2)
C(4)	841(4)	10 029(6)	−1 298(2)
C(5)	476(4)	10 550(5)	−1 689(3)
C(6)	−212(4)	10 158(8)	−1 828(3)
C(7)	−495(4)	9 282(7)	−1 615(3)
C(8)	−105(2)	7 477(4)	−351(2)
C(9)	−153(3)	8 425(6)	− 63(2)
C(10)	173(3)	8 429(5)	398(2)
C(11)	560(3)	7 549(7)	578(2)
C(12)	607(4)	6 524(8)	302(3)
C(13)	250(3)	6 488(5)	−179(2)
C(14)	−2 200(2)	6 483(4)	−1 719(2)
C(15)	−2 381(2)	7 601(5)	−1 901(2)
C(16)	−2 860(3)	7 704(5)	−2 320(2)
C(17)	−3 105(3)	6 758(6)	−2 560(2)
C(18)	−2 939(3)	5 689(6)	−2 396(2)
C(19)	−2 464(3)	5 510(6)	−1 985(2)
C(20)	−2 137(2)	5 551(4)	−770(2)
C(21)	−2 246(3)	4 435(5)	−806(2)
C(22)	−2 643(4)	3 815(6)	−450(3)
C(23)	−2 948(3)	4 449(6)	−100(2)
C(24)	−2 823(4)	5 595(7)	−77(2)
C(25)	−2 419(3)	6 154(5)	−394(2)
C(26)	1 482(3)	6 310(7)	−1 126(2)
C(27)	2 293(3)	5 966(9)	−1 251(3)
C(28)	937(4)	5 676(10)	−2 095(3)
C(29)	898(4)	6 950(11)	−2 236(3)
C(30)	1 062(5)	3 936(8)	−1 337(5)
C(31)	1 252(4)	3 662(8)	−784(4)
O(W)	5 000	2 545(10)	2 500

positions of the different nuclei in the molecule. The $^2J(P^A-P^B)$ values are higher for the Ph_2PNPPh_2 derivatives than for the $Ph_2PCHPPh_2$ compounds. For compound **5c** the couplings P^A-P^B and P^A-P^C are the same, therefore P^A appears as a triplet.

Regarding the ^1H NMR spectra of the $Ph_2PCHPPh_2$ derivatives, it is worth mentioning the resolution of the methylene proton, which appears as a doublet of triplets. This feature can be interpreted as a coupling with P^B [with $^2J(P^B-H) \approx 7.0$ Hz] and a virtual coupling with the two phosphorus atoms in *trans* relative position [with $^2J(P^A-H) \approx 2.0$ Hz].

The crystal structure of $[PdCl(Ph_2PNPPh_2)(PEt_3)]$ **4c** was determined by X-ray diffraction (Fig. 2); it is composed of discrete molecules separated by van der Waals distances. Crystallographic data are given in the Experimental section, atomic coordinates in Table 2 and selected bond distances and angles in Table 3. The compound shows a distorted square-planar co-ordination of Pd: the angles Cl–Pd–P(3) and P(1)–Pd–P(2) are 90.8(1) and 65.2(1)° respectively. It is worth mentioning that the latter angle is the lowest for complexes containing four-membered metallacycles from diphosphines $(Ph_2P)_2Y$, where Y = CH_2 or NH (average values are 73.3 for CH_2 and 70.8° for NH).[8,14] The N atom shows a slight deviation [−0.178(4) Å] from the co-ordination plane formed by Pd, P(1), P(2), P(3) and Cl (plane 1) in accord with the dihedral angle observed, 8.6°, between this plane and the plane of the Ph_2PNPPh_2 ligand (plane 2). The phenyl groups are arranged symmetrically relative to the co-ordination plane: two rings are above it and the other two, below. The palladium–

Table 3 Selected bond lengths (Å) and angles (°) for compound **4c** with e.s.d.s in parentheses

P(1)–Pd	2.244(1)	P(2)–Pd–P(1)	65.2(1)
P(2)–Pd	2.284(1)	P(3)–Pd–P(1)	106.0(1)
P(3)–Pd	2.366(1)	P(3)–Pd–P(2)	170.6(1)
Cl–Pd	2.380(1)	Cl–Pd–P(1)	162.9(1)
N–P(1)	1.653(4)	Cl–Pd–P(2)	97.8(1)
N–P(2)	1.644(4)	Cl–Pd–P(3)	90.8(1)
		P(2)–N–P(1)	95.5(2)

ligand distances are in the range expected. The Pd–P(1) bond is shorter [2.244(1) Å] than Pd–P(2) [2.284(1) Å], consistent with the lower *trans* influence of the chloro ligand. The distances P(1)–N and P(2)–N [1.653(4) and 1.644(4) Å] are shorter than for complexes containing the chelated neutral diphosphine $(Ph_2P)_2NH$ (1.74 Å[8]) which is in accord with delocalization of the negative charge in the anionic ligand $(Ph_2P)_2N^-$. In analogous compounds containing the $Ph_2PCHPPh_2$ methanide ligand the P–C distances are ≈0.1 Å shorter than in the co-ordinated neutral ligand dppm.[15]

It is worth mentioning the short distance between P(1) and P(2) [2.440(1) Å] which is close to a single P–P bond length (for black phosphorus, P–P is 2.38 Å). In palladium complexes containing the neutral dppa ligand the average P–P bond distance is 2.63 Å.[8,14] A decrease is also observed in the angle P(1)–N–P(2) [95.5(2)°] relative to the free ligand (122.8°). These structural features stabilize the four-membered metallacycle in the complex.

Experimental

Infrared spectra were recorded as KBr pellets on a Perkin Elmer 1330 spectrophotometer over the range 4000–200 cm^{-1}, $^{31}P-\{^1H\}$ NMR spectra on a Bruker FT-80 SY spectrophotometer at 32.4 MHz with 85% H_3PO_4 as external standard, and ^1H NMR spectra on a Varian XL-200 or XL-500 instrument with $SiMe_4$ as internal standard. The NMR chemical shifts are expressed as δ values with upfield shifts negative. Chemical analyses (C,H,N) were carried out at the Institut de Química Biorgànica de Barcelona (C.S.I.C.).

Materials and Syntheses.—Bis(diphenylphosphino)methane (dppm)[16] and bis(diphenylphosphino)amine (dppa)[17] were prepared by published methods. The following complexes were prepared by the methods reported: $[MX_2L_2]$ (M = Ni, X = Cl or Br, L = PEt_3, PMe_2Ph or PPh_3;[18] M = Pd, X = Cl, L = PEt_3, PMe_2Ph or PPh_3[19]) and $[MX(R)L_2]$ (M = Ni, R = mesityl;[20] M = Pd, R = mesityl or *o*-tolyl[21]). All new compounds were prepared in a dry nitrogen atmosphere using conventional Schlenk techniques. The solvents were dried and freshly distilled under N_2. The lithiomethanide, $Li[Ph_2PCHPPh_2]$·tmen (tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine),[22] and lithioamide, $Li[Ph_2PNPPh_2]$,[23] were prepared by reaction of the diphosphine with $LiBu^n$, in thf at −15 °C for 1 h. These solutions were used immediately after preparation.

$[PdCl(Ph_2PCHPPh_2)L]$ (L = PPh_3 **1a**, PMe_2Ph **1b** or PEt_3 **1c**). The yellow lithiomethanide solution [0.38 g (1 mmol) dppm and 0.15 cm^3 of tmen (*d* = 0.770 g cm^{-3}) in 10 cm^3 thf was treated with 0.63 cm^3 $LiBu^n$ (*ca.* 1.6 mol dm^{-3} in hexane) at −15 °C for 1 h], $Li[Ph_2PCHPPh_2]$·tmen, was added by syringe at −30 °C to a solution of 1 mmol of $[PdCl_2L_2]$ (0.70 g, L = PPh_3; 0.41 g, PMe_2Ph; 0.45 g, PEt_3). The mixture was warmed slowly to room temperature and stirred for 2 h. The red solution was filtered off and the solvent was removed under reduced pressure. After adding hexane (15 cm^3) an orange precipitate was formed. The products were recrystallized from toluene–hexane. Yields: 0.53 (75) for **1a**, 0.27 (65) for **1b** and 0.31 g (70%) for **1c** (Found: C, 65.2; H, 5.2. Calc. for $C_{43}H_{36}ClP_3Pd$ **1a**: C, 65.60; H, 5.10. Found: C, 59.5; H, 4.8. Calc. for $C_{33}H_{32}ClP_3Pd$ **1b**: C, 59.75; H, 4.85. Found: C, 55.8; H, 5.6. Calc. for $C_{31}H_{36}ClP_3Pd$ **1c**: C, 55.55; H, 5.60%). M.p. (decomposition): 110 (**1a**), 135 (**1b**) and 154–156 °C (**1c**).

$[PdR(Ph_2PCHPPh_2)L]$ (R = *mesityl* **2** *or o-tolyl* **3**; L = PPh_3 **a** *or* PMe_2Ph **b**). (*a*) *From* $[PdCl(Ph_2PCHPPh_2)L]$ (L = PPh_3 *or* PMe_2Ph). The complex $[PdCl(Ph_2PCHPPh_2)L]$ (0.79 g, L = PPh_3; 0.66 g, PMe_2Ph) in thf (15 cm^3) was treated with 10 mmol of MgBr(R) (R = mesityl or *o*-tolyl) solution[21] at − 10 °C. The mixture was warmed to room temperature for 1 h. The solution was filtered off and the solvent removed under reduced pressure. After adding hexane (15 cm^3) an orange precipitate was formed. The products were recrystallized from toluene–hexane. Yields: 0.40 (50) for **2a**, 0.47 (60) for **3a**, 0.36 (55) for **2b** and 0.40 g (60%) for **3b** (Found: C, 57.8; H, 5.4. Calc. for $C_{52}H_{47}P_3Pd$ **2a**: C, 57.90; H, 5.45. Found: C, 71.1; H, 5.0. Calc. for $C_{50}H_{43}P_3Pd$ **3a**: C, 71.25; H, 5.15. Found: C, 67.4; H, 5.5. Calc. for $C_{42}H_{43}P_3Pd$ **2b**: C, 67.55; H, 5.80. Found: C, 66.5; H, 5.8. Calc. for $C_{40}H_{39}P_3Pd$ **3b**: C, 66.85; H, 6.05%. M.p. (decomposition): 100 (**2a**), 120 (**3a**), 105 (**2b**) and 95 °C (**3b**).

(*b*) *From* $[PdBr(R)(PPh_3)_2]$ (R = *mesityl or* o-*tolyl*). The salt $Li[Ph_2PCHPPh_2]$·tmen (1 mmol) at −25 °C was added slowly to a solution of 1 mmol of $[PdBr(R)(PPh_3)_2]$ (0.83 g, R = mesityl; 0.80 g, *o*-tolyl) in thf (25 cm^3). The mixture was warmed slowly to room temperature and stirred for 12 h. The red solution was filtered off and the solvent was removed under reduced pressure. After adding hexane (15 cm^3) an orange precipitate was formed. The products were recrystallized from toluene–hexane. Yields: 0.25 (30) for **2a** and 0.32 g (40%) for **3a**.

(*c*) *From* $[Pd(thf)(C_6H_2Me_3\text{-}2,4,6)(PPh_3)_2]^+$. The salt $Li[Ph_2PCHPPh_2]$·tmen (1 mmol of) at −25 °C was added slowly to a solution of 1 mmol of $[Pd(thf)(C_6H_2Me_3\text{-}2,4,6)(PPh_3)_2]^+$ {0.83 g of $[PdBr(C_6H_2Me_3\text{-}2,4,6)(PPh_3)_2]$ in 20 cm^3 of thf was treated with 0.21 g (1 mmol) of $AgClO_4$ at room temperature for 45 min}. The mixture was warmed to room temperature and stirred for 2 h. The red solution was filtered and the solvent removed under reduced pressure. After adding hexane (15 cm^3) an orange precipitate was formed. The product was recrystallized from toluene–hexane. Yield: 0.42 g (50%).

$[MX(Ph_2PNPPh_2)(PEt_3)]$ (M = Pd, X = Cl **4c**; M = Ni, X = Br **5c**). The yellow lithioamide solution [0.39 g (1 mmol) of dppa in 10 cm^3 of thf was treated with 0.63 cm^3 of $LiBu^n$ (*ca.* 1.6 mol dm^{-3} in hexane) at − 15 °C for 1 h], $Li[Ph_2PNPPh_2]$, was added by syringe at −30 °C to a solution of 1 mmol of $[MX_2(PEt_3)_2]$ (0.41 g for M = Pd, 0.45 g for M = Ni) and PEt_3 (0.2 cm^3) in thf (10 cm^3). The mixture was warmed slowly to −5 °C and stirred for 2 h. The solution was filtered and the solvent removed under reduced pressure. After adding hexane (15 cm^3) a yellow (for palladium) or a red precipitate (for nickel) was formed. These products were recrystallized from toluene–hexane. Yields: 0.27 (65) for **4c** and 0.23 g (50%) for **5c** (Found: C, 55.7; H, 5.5; N, 2.1. Calc. for $C_{30}H_{35}ClNP_3Pd$ **4c**: C, 55.90; H, 5.50; N, 2.15. Found: C, 56.7; H, 5.6; N, 2.1. Calc. for $C_{30}H_{35}BrNNiP_3$ **5c**: C, 56.20; H, 5.50; N, 2.20%). M.p. (decomposition): 177 (**4c**) and 100 °C (**5c**).

$[MX(dppa)(PEt_3)]BF_4$ (M = Pd, X = Cl **6c**; M = Ni, X = Br **7c**). The complex $[MX(Ph_2PNPPh_2)(PEt_3)]$ (0.5 mmol) (M = Ni, X = Br, 0.32 g; M = Pd, X = Cl, 0.32 g) in toluene (20 cm^3) at room temperature was treated with HBF_4 (0.10 cm^3, *ca.* 6.5 mol dm^{-3}), for 1 h. A white solid was formed for the palladium derivative and a red solid for the nickel one. The solids were filtered off and washed with toluene and diethyl ether. Yields: 0.27 (85) for **6c** and 0.24 g (75%) for **7c** (Found: C, 49.0; H, 4.5; N, 1.9. Calc. for $C_{30}H_{36}BClF_4NP_3Pd$ **6c**: C, 49.25; H, 4.95; N, 1.90. Found: C, 49.2; H, 4.7; N, 2.0. Calc. for $C_{30}H_{36}BBrF_4NNiP_3$ **7c**: C, 49.45; H, 5.00; N, 1.90%). M.p. (decomposition): 110 (**6c**) and 133 °C (**7c**).

$[\{Ag(\mu\text{-}Ph_2PNPPh_2)\}_2]$. The salt $Li[Ph_2PNPPh_2]$ (1 mmol) was added slowly to a solution of $AgBF_4$ (1 mmol, 0.20 g) in thf (15 cm^3) at −25 °C. A few minutes later a white solid was formed. The mixture was warmed to room temperature, stirred for 30 min, then filtered. The white solid was washed with thf and acetone. Yield: 0.42 g (85%).

Crystal-structure Determination of Compound **4c**.—*Crystal data*. $C_{30}H_{35}ClNP_3Pd{\cdot}0.5H_2O$, $M = 653.1$, monoclinic, space group $C2/c$, $a = 18.416(6)$, $b = 11.702(4)$, $c = 27.620(9)$ Å, $\beta = 93.50(4)^\circ$, $U = 5941$ Å^3, $D_c = 1.440$ g cm^{-3}, $Z = 8$, $F(000) = 2640$, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 8.84 cm^{-1}, 298 K.

Data collection and processing. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($6 \leqslant \theta \leqslant 12^\circ$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-Kα radiation, using the ω–2θ scan technique. 10 882 Reflections were measured in the range $2 \leqslant \theta \leqslant 30^\circ$, 8697 of which were assumed as observed $[I \geqslant 2.5\sigma(I)]$; R_{int} on F was 0.041. Three reflections were measured every 2 h as orientation and intensity control but significant intensity decay was not observed. Lorentz-polarization but not absorption corrections were made.

Structure analysis and refinement. The structure was solved by Patterson synthesis and refined by the full-matrix least-squares method, using the SHELX 76 computer program.[24] The function minimized was $\Sigma w||F_o| - |F_c|^2$, where $w = \sigma^{-2}(F_o)$; f, f' and f'' were taken from ref. 25. The H atoms were not located. The final R factor was 0.065 ($R' = 0.065$) for all observed reflections; 330 refined parameters. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.4 and −0.4 e Å^{-3}, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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