www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 180–191

Journal of Organometallic Chemistry

Stable alkynyl palladium(II) and nickel(II) complexes with terdentate PNO and PNN hydrazone ligands

Alessia Bacchi [a], Mauro Carcelli [a], Mirco Costa [b], Andrea Fochi [a], Claudio Monici [b], Paolo Pelagatti [a], Corrado Pelizzi [a], Giancarlo Pelizzi [a,*], Luisa Maria Sanjuan Roca [a,1]

[a] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy*

[b] *Dipartimento di Chimica Organica ed Industriale, Università degli Studi di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy*

Received 4 June 1999; accepted 7 September 1999

Abstract

Chloro and acetato complexes of palladium(II) and nickel(II) with terdentate PNO acylhydrazonic ligands derived from 2-(diphenylphosphino)benzaldehyde have been synthesized and characterized. The acetato complexes are able to activate the C–H bond of terminal alkynes, giving stable alkynyl complexes, one of which has been X-ray characterized. The coordination chemistry of the new PNN ligand 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone (**HL6**) has been also investigated and the X-ray crystal structure of the complex [Pd(**HL6**)Cl][Pd**L6**Cl]Cl·$2H_2O$ is reported. Starting from the nickel(II) acetato complex of **HL6**, it has been possible to obtain a new stable alkynyl derivative. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkynyl complexes; Nickel complexes; Palladium complexes; Terdentate ligands; Hydrazone

---

1. Introduction

Recently a considerable interest has been directed towards the synthesis of complexes with terdentate ligands, and their use in organometallic chemistry and homogeneous catalysis is growing [1–3]. As part of our ongoing research on the coordination properties of hydrazones, we undertook the synthesis of terdentate, semi-labile, multifunctional ligands having both hard and soft donor atoms and of their palladium(II) complexes [4]; the reactivity of these compounds towards small molecules as hydrogen [5] and carbon monoxide [6] was also studied. During the hydrogenation of phenylacetylene catalyzed by Pd(**L2**)(CH_3COO) (**HL2** = 2-(diphenylphosphino)benzaldehyde benzoylhydrazone) the alkynylpalladium(II) complex Pd(**L2**)($C{\equiv}C{-}C_6H_5$) was isolated; the same product was also obtained by direct synthesis between Pd(**L2**)(CH_3COO) and phenylacetylene at room temperature [7]. The mild conditions of this reaction are remarkable, in fact most alkynylpalladium(II) complexes were obtained by oxidative addition of an alkynyl halide to a palladium(0) complex or via metathetic substitution between a halopalladium(II) complex and Li($C{\equiv}C{-}R$) [8]. There is a considerable interest in metal complexes incorporating the alkyne moiety, e.g. as material for non-linear optics [9], for luminescence studies [10], and as rigid rod molecular wires [11]. In this context, a set of PNO hydrazone ligands (Scheme 1) and the corresponding palladium(II) complexes (Schemes 1 and 2) were synthesized and their reactivity towards alkynes was studied. The PNN ligand 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone (**HL6**, Scheme 1) was also synthesized, where the carbonyl oxygen donor is replaced by the pyridine nitrogen, but the monoprotic nature of the ligand is retained; its nickel(II) and palladium(II) complexes were characterized and their reactivity towards phenylacetylene was examined.

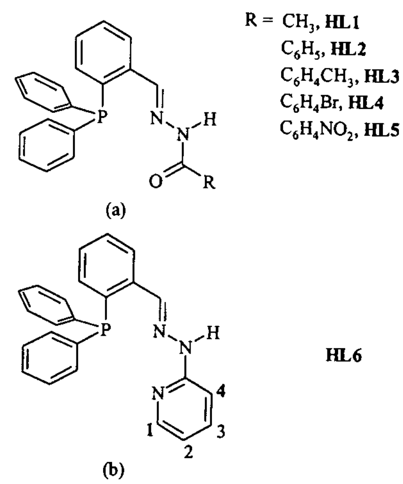
---

[*] Corresponding author. Fax: +39-0521-905557.

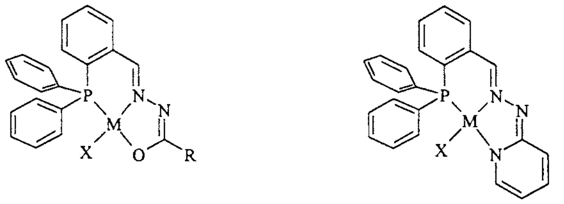
E-mail address: chimic6@ipruniv.cce.unipr.it (G. Pelizzi)

[1] Present address: Departimento de Quimica Inorganica, Universidade de Santiago de Compostela, Av. das Ciencias s/n, A Corunha, Spain.

PII: S0022-328X(99)00519-7



Scheme 1. Presentation of the ligands.



X	Cl	CH3COO	C6H5C≡C	*t*-Bu-C≡C
HL1	1a(Pd)	1b(Pd)	1c(Pd)	
HL2	2a(M)	2b(M)	2c(M)	2d(M)
HL3	3a(Pd)	3b(Pd)	3c(Pd)	
HL4	4a(Pd)	4b(Pd)	4c(Pd)	
HL5	5a(Pd)	5b(Pd)	5c(Pd)	
HL6	6a(M)	6b(M)	6c(M)	

Scheme 2. Structure and annotation for the complexes, M = Ni or Pd.

2. Experimental

All reactions were carried out under nitrogen; the solvents were dried in accordance with literature methods. All reagents of commercial quality were used without further purification, only phenylacetylene was distilled prior to use. Elemental analyses (C, H, N) were carried out on an automatic Carlo Erba CHNS-O EA1108 elemental analyser. All new compounds gave satisfactory elemental analyses. IR spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FTIR spectrometer, mass spectra (CI) on a Finnigan SSQ710 instrument, ^{1}H- and ^{31}P-NMR spectra on a Bruker ACX 300 instrument at 25°C; chemical shifts (δ) are relative to tetramethylsilane (^{1}H-NMR) and H_3PO_4 ($^{31}P\{^1H\}$-NMR). Melting points were obtained with a Gallenkamp MFB-595 apparatus in open capillaries.

The synthesis of the ligands **HL1**–**5** and the corresponding complexes **1b(Pd)**–**5b(Pd)**, **2a(Pd)** and **2c(Pd)** was already described [5,7]; X-ray quality crystals of **2a(Pd)** were obtained by recrystallization from toluene.

2.1. Preparation of the ligand *HL6*

A methanol solution (20 ml) of 2-hydrazinopyridine (0.120 g, 1.1 mmol) and 2-(diphenylphosphino)benzaldehyde (0.318 g, 1.1 mmol) was refluxed for 30 min; the light yellow precipitate was filtered, washed with ethyl ether and dried. Yield 78%; m.p. 201°C. IR (cm^{-1}): ν(NH) 3201_{br}, $\nu(CH_{ar})$ 3053_m, ν(C=N) 1601_s, ν(C–P) 1435_m; ^{1}H-NMR (DMSO-d_6): δ 10.95 (s, D_2O exchangeable, 1H, NH), 8.59 (d, 1H, CH=N, *J*(P–H) 4 Hz), 8.05 (d, 1H, H_1), 7.54 (m, 1H, H_3), 7.45–7.18 (m, 14H), 7.38 (d, 1H, H_4), 6.72 (t, 1H, H_2). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ −13.4 (s).

2.2. Preparation of the complexes

2.2.1. Complexes of the ligands *HL1–HL5*

A solution of the ligand (0.100 g) in dichloromethane (20 ml) was slowly added to a solution containing an equimolar amount of the metal salt (K_2PdCl_4, $NiCl_2\cdot6H_2O$ or $Ni(CH_3COO)_2\cdot4H_2O$) in methanol–water (25:10 ml). The mixture was stirred at room temperature (r.t.) for 3 h, then the yellow organic phase was dried with Na_2SO_4; after slow evaporation of the solvent, a microcrystalline product was isolated.

1a(Pd) — M.p. >320°C. Yield 79%. IR (cm^{-1}): ν(C=N) 1615_{br}, 1518_{vs}, ν(C–P) 1432_m, 1378_w; ^{1}H-NMR (DMSO-d_6): δ 8.58 (d, 1H, CH=N, *J*(P–H) 4 Hz), 8.00 (m, 1H, *J*(*ortho*) 6 Hz), 7.80 (t, 1H, *J*(*ortho*) 7.4 Hz), 7.67–7.53 (m, 11H, Ph), 7.42 (t, 1H, H, *J*(*ortho*) 9.6 Hz), 2.00 (s, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 32.1 (s).

3a(Pd) — M.p. 300°C (dec.). Yield 65%. IR (cm^{-1}): ν(C=N) 1599_{vw}, 1500_{vs}, 1472_s, ν(C–P) 1436_m, 1384_{vs}, 1358_s; ^{1}H-NMR ($CDCl_3$): δ 8.58 (d, 1H, CH=N, *J*(P–H) 4 Hz), 8.28 (d, 2H, *J*(*ortho*) 7.4 Hz), 7.93–7.62 (m, 13H, Ph), 7.56 (t, 1H, *J*(*ortho*) 9.2 Hz), 7.36 (d, 2H, *J*(*ortho*) 7.5 Hz), 2.57 (s, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 32.1 (s).

4a(Pd) — M.p. >300°C. Yield 72%. IR (cm^{-1}): ν(C=N) 1579_w, 1504_{vs}, 1472_m, ν(C–P) 1437_m, 1381_{vs}, 1355_s; ^{1}H-NMR ($CDCl_3$): δ 8.39 (d, 1H, CH=N, *J*(P–H) 4 Hz), 8.06 (d, 2H, *J*(*ortho*) 7.4 Hz), 7.73–7.43 (m, 15H, Ph), 7.37 (t, 1H, *J*(*ortho*) 9 Hz). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 32.2 (s).

5a(Pd) — M.p. 300°C (dec.). Yield 83%. IR (cm^{-1}): ν(C=N) 1610_w, $\nu(NO_2)_{as}$ 1529_{vs}, ν(C–P) 1437_m, 1384_{mw}, $\nu(NO_2)_s$ 1341_{vs}; ^{1}H-NMR (DMSO-d_6): δ 8.50 (d, 1H, CH=N, *J*(P–H) 2.8 Hz), 7.75–7.51 (m, 13H, Ph), 7.40 (t, 1H, *J*(*ortho*) 8 Hz). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 32.5 (s).

2a(Ni) — M.p. 243°C. Yield 60%. IR (cm^{-1}): ν(C=N) 1604_s, 1507_s, 1402_{br}. ^{1}H-NMR ($CDCl_3$): δ 8.42 (s, br, 1H, CH=N), 7.75 (d, 2H, *J*(*ortho*) 7.4 Hz), 7.70–7.31 (m, 17H). X-ray quality crystals were obtained by recrystallization from methanol.

2b(Ni) — M.p. 238–239°C. Yield 75%. IR (cm^{-1}): ν(C=N) 1604_w, ν(COO) 1559_w, 1327_s, 1514_s, 1384_{mw}. ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 19.1 (s).

1c(Pd) — 0.04 g (0.078 mmol) of **2b(Pd)** were dissolved in methanol (20 ml) with 0.09 ml (0.783 mmol) of phenylacetylene. The solution was stirred at r.t. for 5 h. The solvent was removed under reduced pressure and the resulting solution cooled at −20°C for 1 night. An orange solid was filtered and washed with diethyl ether. M.p. 210–211°C. Yield 88%. MS (CI) *m*/*z*: 552 (M^-). IR (cm^{-1}): ν(C≡C) 2112_w, ν(C=N) 1560_{vw}, 1522_{vs}, ν(C–P) 1433_s, 1392_s. ^{1}H-NMR ($CDCl_3$): δ 8.32 (d, 1H, CH=N, *J*(P–H) 2.6 Hz), 7.74–7.38 (m, 14H, Ph), 7.05 (m, 3H, *meta* and *para* in C≡C–C_6H_5), 6.85 (dd, 2H, *ortho* in C≡C–C_6H_5, *J*(*ortho*) 6.6, *J*(*meta*) 4.2 Hz), 2.22 (s, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 34.0 (s).

Analogous procedures were followed for the other alkynyl compounds.

3c(Pd) — A yellow solid precipitated during the reaction. M.p. 232–233°C. Yield 60%. MS (CI) *m*/*z*: 628 (M^-). IR (cm^{-1}): ν(C≡C) 2117_w, ν(C=N) 1614_w, 1492_{vs}, 1471_{vs}, ν(C–P) 1436_m, 1380_{vs}, 1359_s. ^{1}H-NMR ($CDCl_3$): δ 8.50 (d, 1H, CH=N, *J*(P–H) 2.6 Hz), 8.16 (d, 2H, *J*(*ortho*) 8.2 Hz), 7.78–7.36 (m, 14H, Ph), 7.18 (d, 2H, *J*(*ortho*) 8 Hz), 7.07 (dd, 3H, *meta* and *para* in C≡C–C_6H_5, *J*(*ortho*) 5.2, *J*(*meta*) 1.9 Hz), 6.89 (dd, 2H, *ortho* in C≡C–C_6H_5, *J*(*ortho*) 8.6, *J*(*meta*) 2 Hz), 2.38 (s, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 34.3 (s).

4c(Pd) — M.p. 235–237°C. Yield 70%. MS (CI) *m*/*z*: 693 (M^-). IR (cm^{-1}): ν(C≡C) 2117_w, ν(C=N) 1578_w, 1502_{vs}, 1476_{vs}, ν(C–P) 1436_m, 1380_{vs}, 1356_s. ^{1}H-NMR ($CDCl_3$): δ 8.49 (d, 1H, CH=N, *J*(P–H) 2.7 Hz), 8.14 (dd, 2H, *J*(*ortho*) 6.8, *J*(*meta*) 1.7 Hz), 7.77–7.37 (m, 16H, Ph), 7.08 (dd, 3H, *meta* and *para* in C≡C–C_6H_5, *J*(*ortho*) 7.8, *J*(*meta*) 4.1 Hz), 6.89 (dd, 2H, *ortho* in C≡C–C_6H_5, *J*(*ortho*) 6.7, *J*(*meta*) 2.0 Hz). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 34.4 (s).

5c(Pd) — M.p. 263–264°C. Yield 80%. MS (CI) *m*/*z*: 660 (M^-). IR (cm^{-1}): ν(C≡C) 2129_w, ν(C=N) 1596_m, $\nu(NO_2)_{as}$ 1428_{vs}–1485_{mw}, ν(C–P) 1436_m, $\nu(NO_2)_s$ 1380_{mw}–1340_{vs}. ^{1}H-NMR ($CDCl_3$): δ 8.53(5) (d, 1H, CH=N, *J*(P–H) 2.7 Hz), 8.43 (d, 2H), 8.22 (d, 2H), 7.79–7.40 (m, 14H, Ph), 7.09 (m, 3H, *meta* and *para* in C≡C–C_6H_5), 6.90 (m, 2H, *ortho* in C≡C–C_6H_5). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 34.5 (s).

2d(Pd) — M.p. 250–253°C. Yield 70%. MS (CI) *m*/*z*: 594 (M^-). Raman (cm^{-1}) ν(C≡C) 2122. IR (cm^{-1}): ν(C≡C) not observed, $\nu(C–H)_{ar}$ 3055_w, $\nu(C–H)_{alkyl}$ 2964_{vs}, ν(C=N) 1588_m, 1500_{vs}, 1378_{vs}, 1359_s. ^{1}H-NMR ($CDCl_3$): δ 8.45 (d, 1H, CH=N, *J*(P–H) 3 Hz), 8.20 (d, 2H), 7.63–7.32 (m, 19H, Ph), 0.89 (m, 9H, *t*-C_4H_9). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 34.0 (s). X-ray quality crystals were obtained by recrystallization from CH_2Cl_2–ethyl ether.

2c(Ni) — M.p. 225–226°C. Yield 53%. IR (cm^{-1}): ν(C≡C) 2106_s, ν(C=N) 1586_m, 1510_s, 1384_m.

2d(Ni) — M.p. 214–218°C. Yield 46%. IR (cm^{-1}): ν(C≡C) not observed, $\nu(C–H_{ar})$ 3052_w, $\nu(C–H_{alkyl})$ 2924–2854_m, ν(C=N) 1587_m, 1495_{vs}, 1370_s. ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 30.6 (s).

Pd(HL2)Cl$_2$ — 0.070 g of Pd(COD)Cl_2 (0.245 mmol) were added to 0.100 g (0.245 mmol) of **HL2** in THF (20 ml). Instantly, a yellow powder precipitated, which was filtered, washed with ethyl ether and dried. M.p. 180–181°C. Yield 87%. IR (cm^{-1}): $\nu(C–H)_{ar}$ 3055_{br}, ν(C=O) 1707_s, ν(C=N) 1603_m, ν(C–P) 1434. ^{1}H-NMR ($CDCl_3$): δ 10.33 (s, 1H, N–H), 8.53 (d, 2H, Ph), 8.06 (t, 1H), 7.80 (t, 1H), 7.77–7.36 (m, 16H).

[Pd(HL2)Cl](TfO) — 0.044 g (0.17 mmol) of silver trifluoromethanesulfonate in THF (10 ml) were dropped in a CH_2Cl_2 solution (20 ml) of Pd(**HL2**)Cl_2: almost immediately AgCl separated from the reaction. After 2 h AgCl was filtered and ethyl ether added, until a yellow precipitate appeared. M.p. 178°C (dec.). Yield 65%. IR (cm^{-1}): ν(N–H) 3184, $\nu(C–H)_{ar}$ 3053_{br}, ν(C=N) 1604_s, ν(C=O) 1551_s, bands attributable to $CF_3SO_3^-$: 1238, 1221, 1026, 636. ^{1}H-NMR ($CDCl_3$): δ 13.85 (s, br, 1H, N–H), 9.55 (d, 1H, CH=N, *J*(P–H) 3.5 Hz), 8.28–7.43 (m, 19H).

2.2.2. Complexes of the ligand *HL6*

6a1(Pd) — 0.034 g (0.128 mmol) of Li_2PdCl_4 in methanol (20 ml) were added to 0.049 g (0.128 mmol) of **HL6** in dry THF (15 ml), after which the solution turned from yellow to orange. The solution was stirred at r.t. for 1 h, concentrated and then ethyl ether added, until a brown solid was obtained. The solid was washed with ethyl ether and then dried. X-ray quality crystals were obtained directly from the reaction solution. M.p. 86°C (dec.). Yield 86%. IR (cm^{-1}): ν(N–H) 3250_w, $\nu(C–H_{ar})$ 3050, ν(C=N) 1617_s, ν(C–P) 1435_s; ^{1}H-NMR ($CDCl_3$): δ 15.04 (s, 0.5H, N–H), 9.28 (d, 1H, CH=N, *J*(P–H) 2.5 Hz), 8.40 (m, 1H, H_1), 7.88 (t, 1H), 7.75–7.26 (m, 15H), 6.93 (t, 1H). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 29.0 (s).

6a2(Pd) — 0.100 g (0.245 mmol) of **HL6** in dry THF (25 ml) were reacted with an equimolar amount of Pd(COD)Cl_2 (0.077 g). After 30 min a pale yellow solid began to precipitate. The solid was filtered, washed with ethyl ether and dried. M.p. 260°C. Yield 62%. IR (cm^{-1}): ν(N–H) 3175_w, $\nu(C–H_{ar})$ 3052, ν(C=N) 1624_s, ν(C–P) 1437_s; ^{1}H-NMR ($CDCl_3$): δ 15.15 (s, 1H, N–H), 9.35 (d, 1H, CH=N, *J*(P–H) 3 Hz), 8.43 (m, 1H, H_1), 7.91 (m, 1H, H_5), 7.73–7.30 (m, 15H), 6.91 (m, 1H). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 31.1 (s).

6a(Pd) — 0.040 g of **6a1(Pd)** were dissolved in dry THF (15 ml) and an excess of Et_3N added (10:1); the yellow solution became scarlet. After 1 h, Et_3NHCl was removed by filtration, the solution concentrated under vacuum and hexane added until a dark red solid precipitated. The solid was washed with cold water, ethyl ether and then dried. The same result was obtained starting from **6a2(Pd)**. M.p. 233°C. Yield 60%. MS (CI) *m*/*z*: 522 (M^-). IR (cm^{-1}): ν(C–H_{ar}) 3057, ν(C=N) 1609_s, ν(C–P) 1431_s; ^{1}H-NMR ($CDCl_3$): δ 8.45 (d, 1H, CH=N, *J*(P–H) 3 Hz), 8.27 (m, 1H, H_1), 7.69–7.34 (m, 15H), 7.01 (d, 1H), 6.54 (t, 1H, H_2). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 29.2 (s).

6a(Ni) — An equimolar amount of $NiCl_2 \cdot 6H_2O$ in water (10 ml) was added to a solution of **HL6** (0.100 g) in THF (15 ml); when Et_3N was added, the solution became scarlet. After 1 h, the ammonium salt was removed by filtration, the solution concentrated under vacuum and the solid washed with cold water, ethyl ether and then dried. M.p. 212°C (dec.). Yield 40%. MS (CI) *m*/*z*: 476 (M^-). IR (cm^{-1}): ν(C=N) 1604_s, ν(C–P) 1437_s; ^{1}H-NMR ($CDCl_3$): δ 8.62 (s, br, 1H, CH=N), 8.05 (m, 1H, H_1), 7.75–6.98 (m, 15H), 6.55 (s, br, 1H, H_2).

6b(Pd) — (a) 0.102 g of **HL6** were dissolved in THF (20 ml), then 0.068 g of $Pd(CH_3COO)_2$, dissolved in acetonitrile (10 ml), were added. The solution was refluxed for 2 h; a dark red solid precipitated when ethyl ether was added (yield 75%). (b) 0.300 g of **6a(Pd)** were dissolved in THF (15 ml), then an equimolar amount of $Ag(CH_3COO)$ in acetonitrile (10 ml) was added. After 30 min the reaction was stopped, AgCl filtered and the solution concentrated: a dark red solid precipitated when ethyl ether was added (yield 60%). M.p. > 300°C. IR (cm^{-1}): ν(C=N) 1609_s, ν(COO) 1632_s, 1310_s, ν(C–P) 1437_m; ^{1}H-NMR ($CDCl_3$): δ 8.17 (t, 1H), 8.07 (d, 1H), 7.92 (d, 1H), 7.73–7.16, 6.75 (m, 2H), 6.31 (m, 2H), 1.61 (m, 3H). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 27.7(s), 25.0(s).

6b(Ni) — 0.053 g (0.20 mmol) of $Ni(CH_3COO)_2 \cdot 4H_2O$ in methanol (20 ml) were added to 0.076 g (0.020 mmol) of **HL6** in dry THF (15 ml): the solution changed colour from green to red. It was stirred at r.t. for 1 h, concentrated in vacuo and then ethyl ether added, obtaining a solid that was washed with ethyl ether and then dried. M.p. 244°C (dec.). Yield 65%. IR (cm^{-1}): ν(C=N) 1595_s, ν(COO) 1615_m, 1364_s, ν(C–P) 1437_s; in the ^{1}H-NMR spectrum all the peaks were very broad: 8.02–6.89 (m), 6.89 (s), 6.60 (s), 6.24 (s), 1.41 (s, CH_3COO). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 20.0 (s).

6c(Ni) — 0.030 g of **6b(Ni)** (0.061 mmol) in MeOH (15 ml) were reacted with a large excess of phenylacetylene (0.3 ml, 50:1) at r.t. for 24 h. The solution was concentrated and a purple solid obtained by adding ethyl ether. M.p. 138°C (dec.). Yield 61%. MS (CI) *m*/*z*: 540 (M^-). IR (cm^{-1}): ν(C–H)$_{ar}$ 3055_w, ν(C≡C) 2102_w, ν(C=N) 1613_m, ν(C–P) 1434_m. ^{1}H-NMR ($CDCl_3$): δ 8.86 (s, br, 1H, CH=N), 8.56 (s, br, 1H, H_1), 7.76–7.11 (m, 19H), 6.74–6.65 (m, 3H). ^{31}P-NMR ($CDCl_3$, 80 MHz): δ 28.0 (s).

2.3. X-ray crystallography

Crystals suitable for X-ray diffraction analysis have been obtained for compounds **2a(Ni)**, **2d(Pd)**, **6a1(Pd)** and **2a(Pd)**. A summary of relevant parameters concerning data collection and structure refinement for all compounds is reported in Table 1. In all cases the intensity of one standard reflection was monitored through data collection. None of the compounds showed decay effects. The empirical ψ scan correction for absorption was applied for compound **6a1(Pd)**, for compound **2d(Pd)** the Walker and Stuart correction [12] was applied, while no correction for absorption was necessary for **2a(Pd)** and **2a(Ni)**. In all cases the phase problem was solved by direct methods using SIR-97 [13]. Structure refinement was carried out by full matrix least-squares on F^2 using SHELXL-97 [14]. All non hydrogen atoms were refined anisotropically. In compound **2a(Ni)** all hydrogen atoms were located on the difference Fourier map and refined isotropically. In the remaining compounds some or all hydrogen atoms were put in calculated position riding on their carriers. Lists of significant distances and angles are shown in Tables 2–5; all geometrical calculations were carried out with PARST [15], while ZORTEP [16] diagrams of the compounds are shown in Figs. 1, 2, 4 and 5.

2.4. Theoretical calculations

The bond orders and the charge distribution on the bicyclic chelating system of molecules [Pd(**HL6**)Cl]$^+$ and [Pd(**L6**)Cl] in **6a1(Pd)** and of **2a(Pd)** were obtained by extended-Hückel calculations with the program CACAO [17], using the X-ray coordinates as input.

3. Results and discussion

The ligands **HL1**–**HL5** (Scheme 1) react with potassium tetrachloropalladate giving MLCl complexes (Scheme 2, **1a(Pd)**–**5a(Pd)**); the deprotonated ligands behave as terdentate through the phosphorus, the imine nitrogen and the oxygen. The square planar coordination around the metal is completed by a chlorine ion, as shown by X-ray diffraction analysis on **2a(Pd)** (see Section 2.4). The main spectroscopic data of these complexes are: (1) the disappearance of the C=O stretching band, due to the deprotonation of the ligand and the coordination of the oxygen that stabilizes the C–O enolic form; (2) the disappearance of the N–H

Table 1
Crystal and structure refinement data for compounds **6a1(Pd)**, **2a(Pd)**, **2a(Ni)** and **2d(Pd)**

Compound	**6a1(Pd)**	**2a(Pd)**	**2a(Ni)**	**2d(Pd)**
Empirical formula	$C_{48}H_{43}Cl_3N_6O_2P_2Pd_2$	$C_{29.5}H_{24}ClN_2OPPd$	$C_{26}H_{20}ClN_2NiOP$	$C_{32}H_{29}N_2OPPd$
Radiation, λ (Å)	Mo–K_α, 0.7108	Mo–K_α, 0.7108	Mo–K_α, 0.7108	Cu–K_α, 1.5418
Diffractometer	Philips PW1100	Siemens AED	Siemens AED	Enraf–Nonius CAD4
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$C2/c$
Unit cell dimensions				
a (Å)	13.307(5)	10.551(2)	12.160(4)	22.014(2)
b (Å)	15.810(5)	14.251(3)	26.855(8)	18.068(2)
c (Å)	12.590(5)	9.551(2)	14.138(5)	14.476(2)
α (°)	100.43(5)	99.77(2)		
β (°)	101.51(5)	105.10(2)	96.86(2)	102.38(5)
γ (°)	67.66(5)	104.77(2)		
Volume (Å^3)	2384(2)	1297(1)	4584(2)	5694(1)
Z	2	2	8	8
Crystal size (mm)	$0.4\times0.3\times0.2$	$0.5\times0.3\times0.2$	$0.5\times0.4\times0.4$	$0.6\times0.2\times0.1$
Crystal colour	Dark red	Light yellow	Dark red	Pale yellow
θ Range (°)	3–25	3–30	3–30	3–70
Collected reflections	8378	7595	14 148	5561
Independent reflections	8378	7595	13 393	5346
Observed reflections ($I>2\sigma I$)	3158	5024	4054	3383
Parameters/restraints	538/392	378/0	737/0	341/0
Final R indices				
R_1 [a] [$I>2\sigma(I)$]	0.0655	0.0465	0.0505	0.0577
R_w [b]	0.2066	0.1397	0.1519	0.2071

[a] $R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$.

[b] $R_w=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

peak in the ^{1}H-NMR spectrum; (3) the large uppershift of ^{31}P resonance (≈ 40 ppm) upon coordination to the metal. Even if the different R substituents (Scheme 1) modulate the acidic character of the hydrazonic proton [5], they do not influence the course of the complexation reaction and the resulting coordination around the metal.

The deprotonation of the ligand also occurs in the reactions of **HL1**–**HL5** with palladium(II) acetate to give the complexes **1b(Pd)**–**5b(Pd)**. The spectroscopic features are the same along the series (^{31}P chemical shift, position of the acetate bands in the IR spectra) and consequently the coordination already observed in **1b(Pd)** [5] can be assumed for all of these complexes, with the metal bonded to the phosphorus, the imine nitrogen and the oxygen of the ligand and to the monodentate acetate anion.

HL2 reacts with $NiCl_2{\cdot}6H_2O$ or $Ni(CH_3COO)_2{\cdot}4H_2O$, giving **2a(Ni)** and **2b(Ni)**, respectively. The spectroscopic data and the X-ray diffraction analysis on **2a(Ni)** (see Section 4) indicate that the coordination is the same as in palladium chlorides and acetates.

While the palladium and nickel chloro complexes do not react with phenylacetylene or *t*-butylacetylene, the acetato complexes are able to activate the C–H bond of terminal alkynes, giving stable alkynyl complexes; the products were characterized by elemental analyses, IR, ^{1}H- and ^{31}P-NMR spectroscopies and it was also possible to undertake X-ray diffraction analysis of **2d(Pd)** (see Section 4). These compounds are air stable and are recovered unchanged after prolonged refluxing in methanol or toluene. **2c(Pd)** seems to be more stable than **2d(Pd)**, as it can be obtained by refluxing **2d(Pd)** at 50°C in THF with an excess of phenylacetylene. These alkynyl complexes do not undergo oxidative addition or CO insertion into Pd–C bond: a dichloromethane solution of **2c(Pd)** does not adsorb CO at 1 atm nor at 30 atm; the same solution was heated under nitrogen at 40°C with methyl iodide for 2 h, but the starting complex was recovered unaltered.

The ligand 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone (**HL6**) is obtained in good yield by condensation of the aldehyde and 2-hydrazinopyridine; as a solid it is air stable and it has been characterized by means of the usual techniques. In solution a single isomer is detectable by ^{1}H-NMR, probably the *E*-isomer; the imine proton is coupled to the ^{31}P nucleus, as in other 2-(diphenylphosphino)benzaldehyde derivatives [18,19].

In many respects the reactivity of **HL6** is different from that of the acylhydrazonic ligands **HL1**–**HL5**. In fact, it reacts with Li_2PdCl_4 giving a brown solid that has been unequivocally characterized as [Pd(**HL6**)Cl][Pd(**L6**)Cl]Cl·$2H_2O$ (**6a1(Pd)**) (see Section

4): the square planar geometry around the two independent palladium(II) atoms is reached by means of the phosphorus, the imine and the pyridine nitrogens of the ligand, and a chlorine atom; half the molecules of the ligand are deprotonated and an ionic chlorine balances the charge. **HL1**–**HL5** are, evidently, more acidic than **HL6**, since in the same conditions they form neutral PdLCl complexes. Despite its flexibility, **HL6** has a strong tendency to coordinate in a terdentate fashion, as it has been already observed for the related PNN ligand *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine [20]. In fact, in solution the pyridine ring results still coordinated, as can be inferred from the uppershift of the H_1 proton and from the presence of a fine structure for this signal, due to the coupling with the *trans* phosphorous [21] in the ^{1}H-NMR spectrum. Strangely, in the ^{1}H-NMR spectrum of **6a1(Pd)** in $CDCl_3$ at r.t. it is not possible to distinguish two sets of resonances for the deprotonated and neutral ligand, but the N–H peak has half the area corresponding to a proton; only one signal is present in the ^{31}P spectrum (29.0 ppm).

The complex **6a2(Pd)** is easily obtained by reacting **HL6** and $Pd(COD)Cl_2$ in dry THF. The ligand is neutral (ν(N–H) 3175 cm^{-1}; N–H 15.15 ppm) and

Table 2
Selected bond distances (Å) and angles (°) with S.U.S in parentheses for compound **6a1(Pd)**

Pd1–Cl1	2.285(4)	Pd2–Cl2	2.273(3)
Pd1–P1	2.219(3)	Pd2–P2	2.225(4)
Pd1–N1	2.02(1)	Pd2–N4	1.985(9)
Pd1–N3	2.079(9)	Pd2–N6	2.06(1)
P1–C1	1.81(1)	P2–C25	1.79(1)
N1–N2	1.35(2)	N4–N5	1.43(2)
N1–C7	1.32(1)	N4–C31	1.28(2)
N2–C8	1.37(1)	N5–C32	1.35(2)
N3–C8	1.39(2)	N6–C32	1.30(2)
N3–C12	1.33(1)	N6–C36	1.30(2)
C1–C6	1.39(2)	C25–C30	1.43(2)
C6–C7	1.42(2)	C30–C31	1.47(2)
C8–C9	1.37(2)	C32–C33	1.43(3)
Cl1–Pd1–P1	89.0(1)	Cl2–Pd2–P2	90.8(1)
Cl1–Pd1–N1	175.1(3)	Cl2–Pd2–N4	175.3(3)
Cl1–Pd1–N3	95.1(3)	Cl2–Pd2–N6	94.3(4)
P1–Pd1–N1	95.2(3)	P2–Pd2–N4	93.7(4)
P1–Pd1–N3	175.3(3)	P2–Pd2–N6	174.9(4)
N1–Pd1–N3	80.8(4)	N4–Pd2–N6	81.2(5)
Pd1–P1–C1	112.6(4)	Pd2–P2–C25	110.9(5)
C1–P1–C13	104.2(5)	C25–P2–C43	107.3(5)
Pd1–N1–N2	111.7(9)	Pd2–N4–N5	110.3(7)
Pd1–N1–C7	130.9(8)	Pd2–N4–C31	135(1)
N2–N1–C7	117(1)	N5–N4–C31	114(1)
N1–N2–C8	121(1)	N4–N5–C32	116(1)
Pd1–N3–C8	111.5(9)	Pd2–N6–C32	111(1)
P1–C1–C6	123.8(9)	P2–C25–C30	123(1)
C1–C6–C7	129(1)	C25–C30–C31	127(1)
N1–C7–C6	128(1)	N4–C31–C30	125(2)
N2–C8–N3	115(1)	N5–C32–N6	119(2)

Table 3
Selected bond distances (Å) and angles (°) with S.U.S in parentheses for **2a(Pd)**

Pd–P	2.208(1)
Pd–Cl	2.282(1)
Pd–O	2.067(3)
Pd–N1	2.001(2)
P–C1	1.821(3)
O–C8	1.291(3)
N1–N2	1.405(4)
N1–C7	1.257(5)
N2–C8	1.321(5)
C1–C6	1.403(4)
C6–C7	1.473(5)
C8–C9	1.492(6)
P–Pd–Cl	90.06(4)
P–Pd–O	176.26(8)
P–Pd–N1	96.08(8)
Cl–Pd–O	93.31(8)
Cl–Pd–N1	173.47(9)
O–Pd–N1	80.5(1)
Pd–P–C1	111.7(1)
Pd–O–C8	107.9(2)
N2–N1–C7	115.3(3)
N1–N2–C8	112.0(3)
P–C1–C6	123.0(2)
C1–C6–C7	127.8(3)
N1–C7–C6	128.6(3)
O–C8–N2	126.5(3)
O–C8–C9	117.2(3)

Table 4
Selected bond distances (Å) and angles (°) with S.U.S in parentheses for compound **2a(Ni)**

Ni1–P1	2.148(1)	Ni2–P2	2.137(1)
Ni1–Cl1	2.170(1)	Ni2–Cl2	2.154(1)
Ni1–O1	1.878(3)	Ni2–O2	1.881(3)
Ni1–N1	1.861(3)	Ni2–N3	1.847(3)
P1–C1	1.803(4)	P2–C27	1.809(4)
O1–C8	1.287(5)	O2–C34	1.285(5)
N1–N2	1.410(5)	N3–N4	1.422(4)
N1–C7	1.296(5)	N3–C33	1.306(5)
N2–C8	1.309(5)	N4–C34	1.315(5)
C1–C6	1.394(6)	C27–C32	1.400(6)
C6–C7	1.436(6)	C32–C33	1.448(6)
C8–C9	1.479(6)	C34–C35	1.480(5)
P1–Ni1–Cl1	89.90(4)	P2–Ni2–Cl2	89.21(4)
P1–Ni1–O1	173.63(9)	P2–Ni2–O2	175.22(9)
P1–Ni1–N1	95.1(1)	P2–Ni2–N3	94.9(1)
Cl1–Ni1–O1	91.60(9)	Cl2–Ni2–O2	91.70(8)
Cl1–Ni1–N1	174.4(1)	Cl2–Ni2–N3	174.9(1)
O1–Ni1–N1	83.6(1)	O2–Ni2–N3	84.0(1)
Ni1–P1–C1	113.6(1)	Ni2–P2–C27	113.3(1)
Ni1–O1–C8	110.4(2)	Ni2–O2–C34	110.2(2)
Ni1–N1–N2	113.4(2)	Ni2–N3–N4	113.4(2)
Ni1–N1–C7	133.9(3)	Ni2–N3–C33	134.9(3)
N2–N1–C7	112.8(3)	N4–N3–C33	111.8(3)
N1–N2–C8	109.2(3)	N3–N4–C34	108.7(3)
P1–C1–C6	121.0(3)	P2–C27–C32	120.6(3)
C1–C6–C7	125.9(4)	C27–C32–C33	125.9(4)
N1–C7–C6	128.7(4)	N3–C33–C32	127.2(4)
O1–C8–N2	123.3(4)	O2–C34–N4	123.4(3)

again, terdentate: the H$_1$ proton of the pyridine ring is still coupled with phosphorous. The neutral **HL1**–**HL5** PNO ligands show a smaller tendency to behave as terdentate: in **Pd(HL2)Cl$_2$** (Scheme 3), obtained from the reaction of **HL2** with Pd(COD)Cl$_2$, the ligand is neutral but bidentate, the oxygen being outside the coordination sphere (ν(C=O) = 1707 cm^{-1}). The oxygen coordinates the metal in **[Pd(HL2)Cl](TfO)** (ν(C=O) = 1551 cm^{-1} [22,23]), where one chloride is substituted by a triflate, whose poor coordinating ability is well known.

Table 5
Selected bond distances (Å) and angles (°) with S.U.S in parentheses for compound **2d(Pd)**

Pd–P	2.194(2)
Pd–O	2.069(5)
Pd–N1	2.028(7)
Pd–C27	1.99(1)
P–C1	1.831(8)
O–C8	1.29(1)
N1–N2	1.406(9)
N1–C7	1.27(1)
N2–C8	1.30(1)
C1–C6	1.42(1)
C6–C7	1.44(1)
C8–C9	1.50(1)
C27–C28	1.17(1)
C28–C29	1.49(1)
P–Pd–O	174.8(1)
P–Pd–N1	96.0(2)
P–Pd–C27	88.5(2)
O–Pd–N1	79.0(2)
O–Pd–C27	96.6(3)
N1–Pd–C27	173.8(3)
Pd–P–C1	111.7(2)
Pd–O–C8	108.3(5)
Pd–N1–N2	114.0(5)
Pd–N1–C7	131.8(6)
N2–N1–C7	114.1(6)
N1–N2–C8	110.6(7)
P–C1–C6	123.9(6)
C1–C6–C7	127.9(7)
N1–C7–C6	128.4(8)
O–C8–N2	128.0(8)

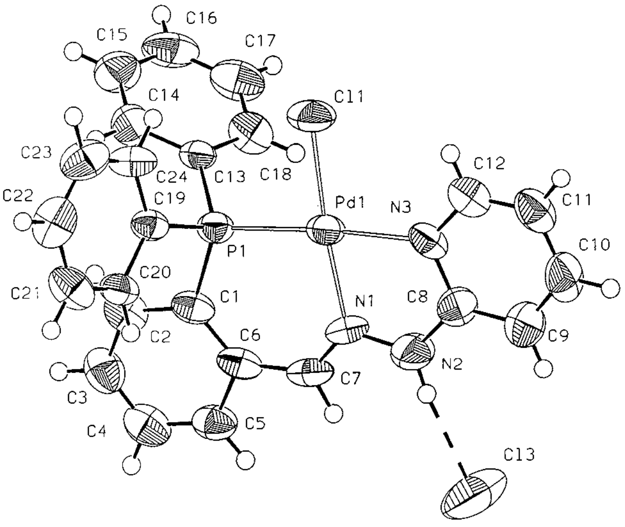


Fig. 1. Perspective view of [Pd(**HL6**)Cl]$^+$, with thermal ellipsoids at 50% probability level. Hydrogen bond N–H···Cl is shown in dashed style.

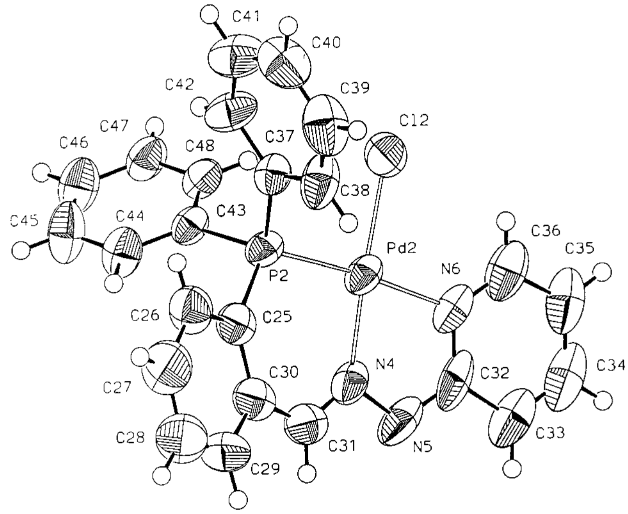
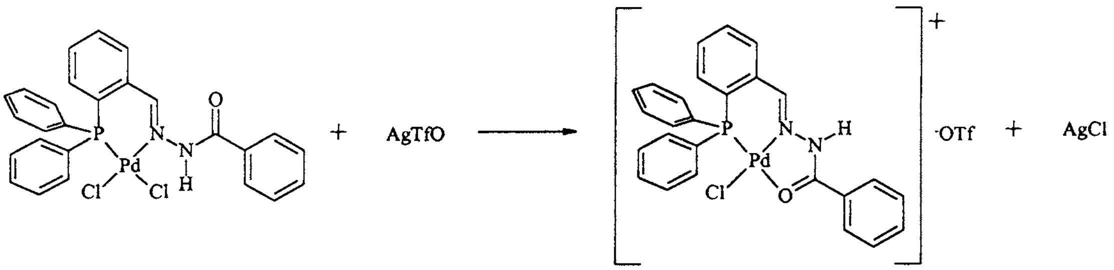


Fig. 2. Perspective view of [Pd(**L6**)Cl], with thermal ellipsoids at 50% probability level.

6a(Pd) is obtained by refluxing **6a1(Pd)** or **6a2(Pd)** with Et$_3$N in THF. The new compound has been characterized by IR, ^{1}H- and ^{31}P-NMR spectroscopies, and all the data suggest the deprotonation of the ligand; the coordination geometry of the starting complexes is retained. It is interesting to compare the UV–vis absorption spectra of **6a(Pd)**, **6a1(Pd)** and **6a2(Pd)**; while in **6a2(Pd)** and **6a(Pd)** the lower energy band is well resolved, in methanol the maximum being at 397 and 528 nm, respectively, the spectrum of **6a1(Pd)** is more complex and, besides a band with a maximum at 528 nm, there is another, less resolved, band near 400 nm.

The corresponding complex **6a(Ni)** was directly synthesized by stirring NiCl$_2$·6H$_2$O, **HL6** and Et$_3$N in THF. **6a(Pd)** and **6a(Ni)**, as the chloro complexes of **HL1**–**HL5**, do not react with phenylacetylene.

After the work-up of the reaction between **HL6** and Pd(CH$_3$COO)$_2$, the complex **6b(Pd)** is isolated: the IR and ^{1}H-NMR spectra indicate the presence of the acetate ion and the absence of hydrazino protons; in the ^{31}P spectrum there are two peaks (27.8 and 25.2 ppm) and in the ^{1}H-NMR spectrum it seems possible to recognize pyridine nitrogens which are coupled with ^{31}P and others which, even if coordinated to the metal, are not coupled. The multidentate nature of the ligand and its flexibility make difficult to propose a plausible structure for **6b(Pd)**. The acetato complex could be also obtained by methatesis from CH$_3$COOAg and **6a(Pd)**,



Scheme 3. The reaction between **Pd(HL2)Cl$_2$** and AgTfO to give **[Pd(HL2)]OTf**.

starting, in this way, with the ligand preorganised, terdentate around the palladium, but, surprisingly, the product of the reaction is again **6b(Pd)**.

On the contrary, **6b(Ni)**, which was obtained by the direct synthesis between Ni(CH$_3$COO)$_2$ and **HL6**, presents the already-described monometallic structure, with the deprotonated terdentate ligand and the anion that completes the square planar coordination around the metal atom. **6b(Ni)** reacts with phenylacetylene giving the corresponding alkynyl complex **6c(Ni)**.

4. X-ray crystal structures

The strong tendency of **HL6** to act as terdentate is confirmed by the X-ray diffraction analysis carried on **6a1(Pd)**. Both neutral and anionic monodeprotonated forms of **HL6** are capable of complexing palladium by acting as PNN terdentate ligands and by completing the metal coordination sphere with a chlorine atom, to give a cationic [Pd(**HL6**)Cl]$^+$ and a neutral [Pd(**L6**)Cl] complex, respectively. Interestingly, these two different forms cocrystallize giving the compound **6a1(Pd)**. A chloride anion and four disordered waters with 50% occupancy complete the unit cell content. Figs. 1 and 2 show perspective views of the molecular structure of [Pd(**HL6**)Cl]Cl and [Pd(**L6**)Cl], respectively, in the crystals of **6a1(Pd)**, along with the labelling scheme. Table 2 lists the main bond distances and angles in the structure. In both moieties the ligand chelates the metal by the imine nitrogen, the pyridine nitrogen, and the phosphorous atoms, originating a six-membered and a five-membered chelation ring; a chlorine completes the square geometry around the palladium and in both cases the coordination is planar within 0.08 Å. The only relevant angular distortion from a regular square is due to the strain of the five-membered chelation ring, giving a significant deviation from 90° of the angles involving the imine and the pyridine nitrogens (N–Pd–N = 80.8(4) and 81.2(5)°, respectively for [Pd(**HL6**)Cl]Cl and [Pd(**L6**)Cl]). The comparison of the two molecules is helpful in elucidating the effects of the deprotonation of the ligand on the complex geometry. The deprotonation of the ligand does not affect significantly the bond lengths in the coordination sphere, apart from a slight shortening of the bond between palladium and the imine nitrogen: Pd1–N1 = 2.02(1) Å for the cationic complex and Pd2–N4 = 1.985(9) Å for the neutral complex. The analysis of the bond lengths along the two chelation rings for the protonated complex [Pd(**HL6**)Cl]$^+$ shows that there is a certain degree of resonance along the system C7–N1–N2–C8–N3 (C7–N1 = 1.32(1), N1–N2 = 1.35(2), N2–C8 = 1.37(1), C8–N3 = 1.39(2), N3–C12 = 1.33(1) Å). This is consistent with the values observed for analogous pyridine-2-carbaldehyde 2′-pyridylhydrazone complexes, where the following ranges are found: C7–N1 = 1.252–1.321, N1–N2 = 1.318–1.358, N2–C8 = 1.374–1.406, C8–N3 = 1.328–1.344, N3–C12 = 1.334–1.362 Å [24–26]. The deprotonation of the hydrazonic nitrogen causes a relevant rearrangement of the bond lengths and a redistribution of the charge on the hydrazonic system. The examination of the bond lengths observed for [Pd(**L6**)Cl] suggests that the electronic density delocalization is shifted from the C=N–N group towards the pyridine ring (C31–N4 = 1.28(2), N4–N5 = 1.43(2), N5–C32 = 1.35(2), C32–N6 = 1.30(2), N6–C36 = 1.30(2) Å). Similar single-bond N–N distance (1.396 Å) and C–N shortening (1.302 Å) have been observed for a nickel complex of (1,10-phenanthrolin-2-yl)benzaldehyde hydrazone [27], where the possibility of charge delocalization on the phenanthroline system is even more effective than in the present pyridine ring. In order to support this observation, an estimation of the partial atomic charges and of bond orders for the crystal structures of [Pd(**HL6**)Cl]Cl and [Pd(**L6**)Cl] has been performed by means of extended-Hückel calculations. The results are shown in Fig. 3. It is seen that the negative charge left on the ligand by the deprotonation is mainly located on the hydrazonic nitrogen N5, but it is also in part distributed on C33 and C35, which result more negative than in the cationic complex. The palladium atom is also slightly less positively charged, and this could be due to the higher bond order between the metal and the imine nitrogen Pd–N4, related to a diminution of the negative charge on N4. Interestingly, the augmented negative charge on the pyridine ring has no effects on the Pd–N(py) bond, which remains un-

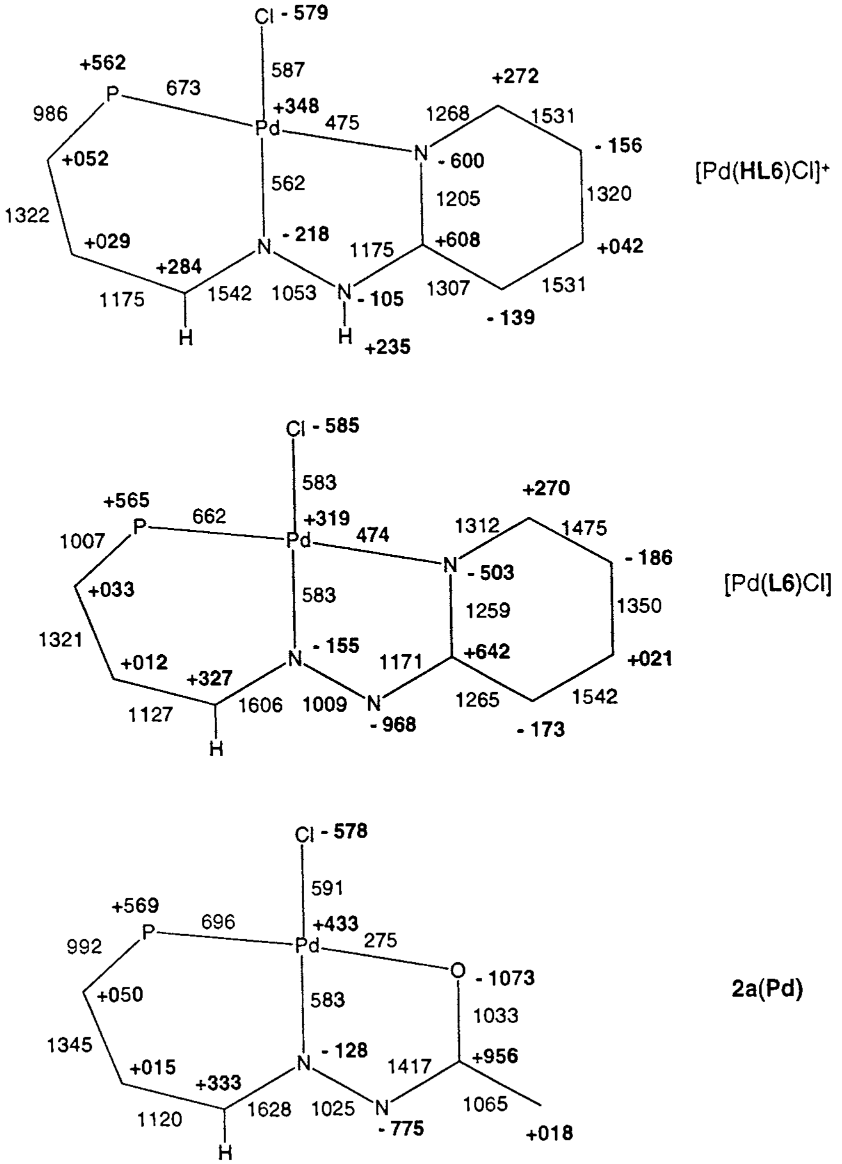


Fig. 3. Atomic partial charges (bold characters, × 1000) and bond orders (× 1000) for the chelation systems in the two moieties of **6a1(Pd)** ([Pd(**HL6**)Cl]$^+$ and [Pd(**L6**)Cl]) and in **2a(Pd)**.

changed, although the pyridine nitrogen appears less negatively charged than in the protonated complex. The partial charges and bond orders on the phosphine–imine moiety of **6a1(Pd)** are substantially unaffected by the deprotonation of the ligand; moreover the C=N bond has a more pronounced multiple character in [Pd(**L6**)Cl], showing that the negative charge is not delocalized along the six-membered chelation ring. The conformational analysis for both molecules shows that in the cationic complex the chelation system comprising atoms Pd1, P1, N1–N3, C1–C12 is planar within 0.20 Å, while in the neutral complex the planarity is perturbed by torsions of 10° around the bonds C25–C30 and C30–C31, compared to values of 2° observed for [Pd(**HL6**)Cl]$^+$. The positive charge of the cationic complex is balanced in the crystal by a chloride anion, which is hydrogen bonded to the hydrazonic N–H, as shown in Fig. 1 (N2···Cl3 = 3.07(1) Å, N–H···Cl = 167(1)°).

The role of the pyridine ring on the negative charge delocalization observed on the ligand backbone of [Pd(**HL6**)Cl] has been compared with the one shown by the phenylacyl group in **2a(Pd)**; in the crystal packing of **2a(Pd)** one toluene molecule is disordered around a

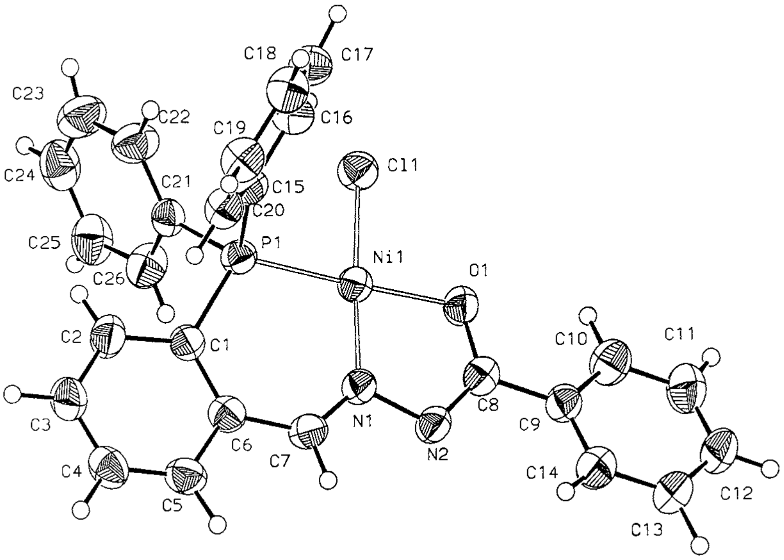


Fig. 4. Perspective view of **2a(Ni)**, with thermal ellipsoids at 50% probability level.

centre of inversion[2]. Relevant bond distances and angles are reported in Table 3; for labelling, refer to the analogue nickel complex in Fig. 4. The charge distribution and bond orders of **2a(Pd)** are shown in Fig. 3. The main differences with respect to the 2-pyridylhydrazone ligand consist in the significantly higher bond order of the N2–C8 bond, accompanied by a large decrease of the bond order C8–O. The electronic density is transferred from the hydrazonic nitrogen to the oxygen, and C8 is highly positive. The higher electronegativity of O with respect to N allows the location of the negative charge on the oxygen, leaving the metal more positive and decreasing the Pd–O bond order.

The analogue nickel complex **2a(Ni)** crystallizes with two independent molecules in the asymmetric unit; one of them is shown in Fig. 4, along with the labelling scheme. As expected, the **L2**$^-$ anion coordinates the metal in a square planar fashion and the coordination is completed by a Cl atom *trans* to the imine nitrogen. The planar coordination is slightly distorted as P1 and P2 deviate by 0.23 and 0.17 Å, respectively, from the plane defined by Ni, Cl, O and hydrazonic N atoms. As seen from Table 4, that lists the relevant geometric parameters for **2a(Ni)**, there are not significant differences in the bonding geometry of the chelation rings between the two molecules. The most evident differences between the nickel and the palladium complexes are due to the steric strain introduced in the chelation rings by the smaller dimensions of the former ion: in the six-membered chelated ring the endocyclic angles on metal, C1 and C6 are of about 2° smaller than in the corresponding palladium complex, while the angles on P1 and N1 are of about 2° larger. This is also associated to a slight but significant shortening of the P1–C1 and C6–C7 bonds in the nickel complex. In the five-membered chelation ring, the endocyclic angles on metal and O are of 4 and 2° larger, respectively, in the Ni complex, while those on C8 and N2 are of about 3° smaller. The examination of the Ni–N and Ni–O distances in complexes containing the same five-membered chelation ring as **2a(Ni)** reveals that the Ni–N distances fall well in the range observed for similar compounds

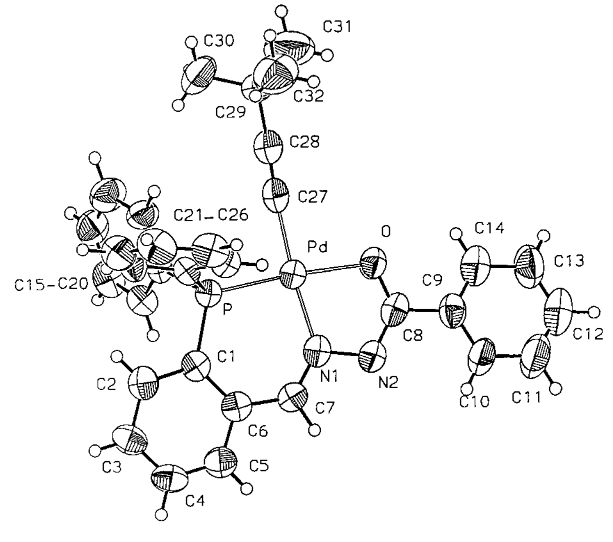


Fig. 5. Perspective view of **2d(Pd)**, with thermal ellipsoids at 50% probability level.

---

[2] The crystal structure of the same compound as a dichloromethane solvate, has been previously reported [7]. The molecular dimensions of the complex are perfectly comparable in the two solvate forms. The only differences are a rotation of 12° of the terminal phenyl around the C8–C9 bond in the toluene solvate, which causes a larger deviation from planarity (maximum deviation = 0.40 Å) of the chelation system Pd, P1, N1–N3, C1–C14 with respect to the one observed in Ref. [7] (maximum deviation = 0.15 Å), and a different orientation of the two phenyl rings bonded to the P atoms.

(1.828–1.910 Å), while the Ni–O distances are sensitive to the *trans* effect of the phosphine group, falling on the upper limit of the range observed (1.833–1.889 Å), as also observed in (thiodibenzoylmethane benzoylhydrazonato)-triphenylphosphine-nickel(II) [28], where the oxygen is *trans* to the sulphur atom. The Ni–P bond lengths are comparable with the one observed in [Ni(acac)(PPh_3)(CH_3CH_2)] [29] (2.143 Å), where the P atom is *trans* to an acetylacetonato oxygen.

In **2d(Pd)** (Fig. 5) the acetylenic ligand is situated *trans* to the imine nitrogen, as already observed in the analogue Ph–C≡C complex [7]. Table 5 lists the main bond distances and angles for **2d(Pd)**. The comparison with the chloro complex shows that there are no relevant differences in the bonding geometry of the two chelation rings. The coordination of the metal is planar within 0.07 Å, and the same applies for the two chelation rings. The overall planarity of the molecular system Pd, P, N1, N2, O, C1–C14 is perturbed by a slight rotation of the terminal phenyl around the C8–C9 bond (O–C8–C9–C14 = −15(1)°), as also observed for **2a(Pd)**. The Pd–N distance is affected by the substitution of the group in the *trans* position and it is longer in the alkynyl than in the chloro complex (2.028(7) and 2.001(2) Å, respectively); a slight shortening of the Pd–P bond is also observed in **2d(Pd)**, 2.194(2) compared to 2.208(1) Å in **2a(Pd)**. The Pd–O, C8–O, and C8–N2 distances do not differ from those observed in **2a(Pd)**, showing that the enolate Pd–O–C=N– form is a major contribution in the electronic distribution on the Pd–O–C–N system, as already evidenced by the calculation of bond orders (Fig. 3). This is also in agreement with the values observed for the crystal structure of a palladium complex with the enolate form of a similar amide phosphine ligand (Pd–O = 2.108(4), C–O = 1.302(5) Å) [30]. The coordination of the acetylenic group is practically linear, with angles of 175.7(9) and 178(1)° on C27 and C28, respectively. The comparison of the geometry of *t*-Bu–C≡C and Ph–C≡C in the two complexes shows that the presence of the alkyl instead of the aryl induces a shortening of the Pd–C bond (1.99(1) and 2.026(4) Å, respectively) and a lengthening of the C≡C bond (1.17(1) and 1.092(6) Å, respectively), as a result of the different electronic characteristics of the two ligands.

5. Conclusions

A procedure for the synthesis of stable acetylides was found, starting from acetato complexes of terdentate hydrazone ligands. The acetato anion plays a key role in the process, in fact the corresponding chloro complexes are not reactive. The mild conditions of the reaction make appealing the possibility to extend this method to di- and tri-functional acetylenes to obtain organometallic species with the metal centres separated by conjugated organic fragments, which are of interest in the area of material and supramolecular chemistry.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 123605 for **2a(Pd)**, 123603 for **2a(Ni)**, 123602 for **2d(Pd)** and 123604 for **6a1(Pd)**.

Acknowledgements

Thanks are due to the Centro di Studio per la Strutturistica Diffrattometrica del CNR and Centro Interfacoltà Misure ‘Giuseppe Casnati’ of the University of Parma.

References

[1] J.H. Groen, A. de Zwart, M.J.M. Vlaar, J.M. Ernsting, P.W.N.M. van Leeuwen, K. Vrieze, H. Kooijman, W.J.J. Smeets, A.L. Spek, P.H.M. Budzelaar, Q. Xiang, R.P. Thummel, Eur. J. Inorg. Chem. (1998) 1129.

[2] M. Yang, M. Alvarez, N. Lugan, R. Mathieu, J. Chem. Soc. Chem. Commun. (1995) 1721.

[3] Y. Kataoka, Y. Tsuji, O. Matsumoto, M. Ohashi, T. Yamagata, K. Tani, J. Chem. Soc. Chem. Commun. (1995) 2099.

[4] A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Chem. Soc. Dalton Trans. (1996) 4239.

[5] P. Pelagatti, A. Bacchi, M. Carcelli, M. Costa, A. Fochi, P. Ghidini, E. Leporati, M. Masi, C. Pelizzi, G. Pelizzi, J. Organomet. Chem. 583 (1999) 94.

[6] P. Pelagatti, M. Carcelli, F. Franchi, C. Pelizzi, A. Bacchi, A. Fochi, H.-W. Frühauf, K. Goubitz, K. Vrieze, Eur. J. Inorg. Chem. in press.

[7] A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, Gazz. Chim. Ital. 124 (1994) 429.

[8] H.F. Klein, B. Zettel, U. Flörke, H.J. Haupt, Chem. Ber. 125 (1992) 9.

[9] J.T. Lin, J.J. Wu, C. Li, Y.S. Wen, K.-J. Lin, Organometallics 15 (1996) 5028.

[10] M.J. Irwin, J.J. Vittal, R.J. Puddephatt, Organometallics 16 (1997) 3541.

[11] V.W.-Wah Yam, W.K.-M. Fung, K.M.-Ch. Wong, V.C-Y. Lau, K.-K. Cheung, J. Chem. Soc. Chem. Commun. (1998) 777.

[12] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.

[13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.

[14] G. Sheldrick, SHELXL-97, Program for structure refinement, University of Göttingen, Germany, 1997.

[15] M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659.

[16] L. Zsolnai, H. Pritzkow, ZORTEP. ORTEP original program modified for PC, University of Heidelberg, Germany, 1994.

[17] C. Mealli, D.M. Proserpio, J. Chem. Educ. 67 (1990) 399.

[18] R.E. Rulke, V.E. Kaasjager, P. Wehman, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, Organometallics 15 (1996) 3022.

[19] A. Bacchi, M. Carcelli, M. Costa, A. Leporati, E. Leporati, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Organomet. Chem. 535 (1997) 107.

[20] P. Wehman, R.E. Rulke, V.E. Kaasjager, P.C.J. Kamer, H. Kooijman, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, J. Chem. Soc. Chem. Commun. (1995) 331.

[21] M. Yabuta, S. Nakamura, T. Yamagata, K. Tani, Chem. Lett. (1993) 323.

[22] J. Andrieu, P. Braunstein, A.D. Burrows, J. Chem. Res. (1993) 380.

[23] M.J. Green, G.J.P. Britovsek, K.J. Cavell, F. Gerhards, B.F. Yates, K. Frankcombe, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1998) 1137.

[24] T. Rojo, J.L. Mesa, M.I. Arriortua, J.M. Savariault, J. Galy, G. Villeneuve, D. Beltran, Inorg. Chem. 27 (1988) 3904.

[25] E.W. Ainscough, A.M. Brodie, S.L. Ingham, J.M. Waters, Inorg. Chim. Acta 249 (1996) 47.

[26] J.L. Mesa, T. Rojo, M.L. Arriortua, G. Villeneuve, J.V. Folgado, A. Beltran-Porter, D. Beltran-Porter, J. Chem. Soc. Dalton Trans. (1989) 53.

[27] S. Choudhury, J. Bangladesh Acad. Sci. 21 (1997) 61.

[28] H. Kraudelt, U. Schilde, E. Uhlemann, F. Weller, Z. Naturforsch. Teil B 52 (1997) 1043.

[29] F.A. Cotton, B.A. Frenz, D.L. Hunter, J. Am. Chem. Soc. 96 (1974) 4820.

[30] J. Andrieu, P. Braunstein, A. Tiripicchio, F. Ugozzoli, Inorg. Chem. 35 (1996) 5975.