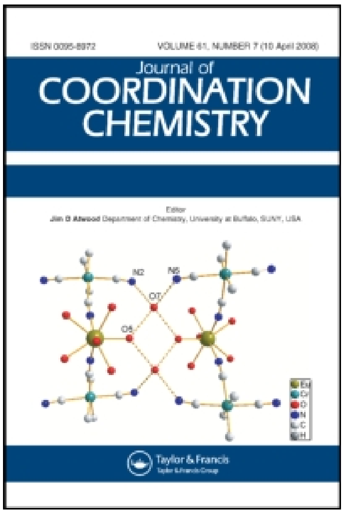

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Chelating Properties of Secondary Alkylphosphite and Alkylphosphonate Palladium(II) Complexes

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To cite this Article Valderrama, M. , Scotti, M. and Abugoch, L.(1990) 'Synthesis and Chelating Properties of Secondary Alkylphosphite and Alkylphosphonate Palladium(II) Complexes', Journal of Coordination Chemistry, 21: 1, 55 — 62
To link to this Article: DOI: 10.1080/00958979009408183
URL: http://dx.doi.org/10.1080/00958979009408183

J. Coord. Chem. 1990, Vol. 21, pp. 55–62
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SYNTHESIS AND CHELATING PROPERTIES OF SECONDARY ALKYLPHOSPHITE AND ALKYLPHOSPHONATE PALLADIUM(II) COMPLEXES

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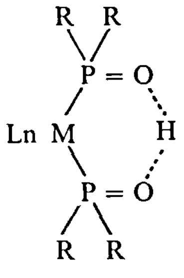
(Received May 25, 1989)

The preparation and properties of new neutral and cationic bis(dialkylphosphonate)palladium(II) complexes of the types $[R'_3P)ClPd\{P(O)(OR)_2\}_2H]$ (R = Me, Et; R′ = Et, Ph) and $[L_2Pd\{P(O)(OR)_2\}_2H]$ A (L_2 = dppe; bipy; R = Me, Et; A = PF_6^-, ClO_4^-) are described. The properties as chelating ligands of the binuclear complex $[PdCl\{P(O)(OEt)_2\}_2H]_2$ and the novel complexes described in the formation of heterometallic palladium(II)–rhodium(I) compounds have been studied. IR, ^1H NMR and ^{31}P NMR spectroscopic data for the isolated complexes are discussed.

Keywords: Palladium(II), alkylphosphites, alkylphosphonates, rhodium(I), synthesis

INTRODUCTION

Several derivatives of transition metals containing disubstituted phosphonito or phosphonate and disubstituted phosphinous acid or phosphite as ligand (of type **1**) have been described.[1–6]



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R = Ph, OPh, OEt, OMe

Recent studies have shown that the hydrogen-bonded proton of these compounds can be easily removed thus forming an anionic complex which can act as a chelating ligand and which may be regarded as an analogue of β-diketonates. A variety of bimetallic derivatives have been reported and the formation of the heterometallocycle was confirmed by X-ray diffraction studies.[5,7] In the reaction of the binuclear complex $[PdCl\{P(O)(OMe)_2\}_2H]_2$ with $[Rh(OMe)COD]_2$ or [Rh(acac)COD], the palladium complex shows different behaviour and the reaction gave an unexpected

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heterotrinuclear complex that contains a novel heterometallic mixed phosphonate-chlorine bridge.[8]

In this article we describe the synthesis and characterization of new neutral or cationic bis(dialkylphosphonate)palladium(II) complexes and their properties as ligands in the formation of heterometallic palladium–rhodium compounds.

EXPERIMENTAL

C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyser. IR spectra were recorded on a Perkin-Elmer 567 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured at 20°C in *ca* 5×10^{-3} M acetone solutions using a WTW LF-521 conductimeter. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer and ^{31}P NMR (proton decoupled) on a Bruker WH-90 instrument. The chemical shifts are reported relative to Me_4Si and 85% H_3PO_4, respectively.

All reactions were carried out in Schlenk tubes under purified nitrogen. Solvents were dried and distilled before use. The starting binuclear complexes $[PdCl\{P(O)(OR)_2\}_2H]_2$ and $[RhCl(COD)]_2$ were prepared by published procedures.[9,10]

$[LClPd\{P(O)(OR)_2\}_2H]$ ($L = PEt_3, PPh_3$; $R = Me, Et$) (I-IV)

To a solution of the complex $[PdCl\{P(O)(OR)_2\}_2H]_2$ (0.3 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise the stoichiometric amount (0.6 mol) of the appropriate phosphine in CH_2Cl_2 solution. The resulting mixture was stirred for 60 min, vacuum concentrated to a small volume and a microcrystalline white solid was precipitated by addition of *n*-pentane.

$[(Et_3P(ClPd\{P(O)(OMe)_2\}_2H]$ (I): Yield 195 mg (68%). Anal.: Calcd. for $C_{10}H_{28}ClO_6P_3Pd$: C, 25.07; H, 5.89%. Found: C, 25.17; H, 5.80%. ^1H NMR ($CDCl_3$): δ15.5 (s,br,OH), 3.81 (d,OCH_3, $^3J(P–H) = 13Hz$), 3.66 (d,OCH_3, $^3J(P–H) = 13Hz$), 2.0 (m,CH_2), 1.1 (m,CH_3) ppm.

$[(Et_3P)ClP\{P(O)(OEt)_2\}_2H]$ (II): Yield 202 mg (63%). Anal.: Calcd. for $C_{14}H_{36}ClO_6P_3Pd$: C, 31.42; H, 6.78%. Found: C, 31.51, H, 7.00%. ^1H NMR ($CDCl_3$): δ4.18 (m,CH_2,OEt), 1.35 (t,CH_3,OEt, $^3J(H–H) = 7Hz$), 1.32 (t,CH_3, OEt, $^3J(H–H) = 7Hz$), 2.06 (m,CH_3,Et), 1.15 (m,CH_3,Et) ppm.

$[(Ph_3P)ClPd\{P(O)(OMe)_2\}_2H]$ (III): Yield 333 mg (89%). Anal.: Calcd. for $C_{22}H_{28}ClO_6P_3Pd$: C, 42.39; H, 4.55%. Found: C, 42.74; H, 4.79%. ^1H NMR ($CDCl_3$): δ12.2 (s,br,OH), 3.84 (d,OCH_3, $^3J(P–H) = 13Hz$), 3.27 (d,OCH_3, $^3J(P–H) = 13Hz$), 7.65 (m,H-ring), 7.42 (s,br,H-ring) ppm.

$[(Ph_3P)ClPd\{P(O)(OEt)_2\}_2H]$ (IV): Yield 167 mg (41%). Anal.: Calcd. for $C_{26}H_{36}ClO_6P_3Pd$: C, 46.03; H, 5.20%. Found: C, 46.30; H, 5.70%. ^1H NMR ($CDCl_3$): δ3.40–4.00 (m,CH_2, OEt), 1.37 (t,CH_3, OEt, $^3J(H–H) = 7Hz$), 1.00 (t,CH_3, OEt, $^3J(H–H) = 7Hz$), 7.56 (m,H-ring) ppm.

$[(bipy)PdCl\{P(O)(OEt)_2\}]$ (V)

To a solution of $[PdCl\{P(O)(OEt)_2\}_2H]_2$ (167 mg; 0.2 mmol), in Me_2CO (10 cm^3) was added dropwise a solution of bipy (62 mg; 0.4 mmol) in acetone (5 cm^3)-dichloromethane (1 cm^3). The mixture was stirred at room temperature for 48 h. The solution was evaporated and the product crystallized upon adding diethylether. Yield 56 mg (32%). Anal.: Calcd. for $C_{14}H_{18}ClN_2O_3PPd$: C, 38.64; H, 4.17; N, 6.44%, Found: C, 38.45; H, 4.06; N, 6.29%.

$[L_2Pd\{P(O)(OR)_2\}_2H]PF_6$ (L_2 = dppe, bipy; R = Me, Et) (VI–IX)

A solution of $[PdCl\{P(O)(OR)_2\}_2H]_2$ (0.2 mmol) in 15 cm^3 of Me_2CO was treated with $AgPF_6$ (101.2 mg; 0.4 mmol). The mixture was stirred for 30 min in the absence of light and the AgCl formed was filtered off through kieselguhr. To the colourless filtrate containing the solvated complex $[\{Me_2CO\}_xPd\{P(O)(OMe)_2\}_2H]^+$ was added dropwise a solution of L_2 (0.4 mmol) in CH_2Cl_2 (5 cm^3). The resulting solution was stirred for 2 h, filtered, vacuum concentrated and the complexes precipitated by addition of diethyl ether (perchlorate complexes were obtained using $AgClO_4$).

$[(dppe)Pd\{P(O)(OMe)_2\}_2H]PF_6$ (VI): Yield 105 mg (60%). Anal.: Calcd. for $C_{30}H_{37}F_6O_6P_5Pd$: C, 41.46; H, 4.29%. Found: C, 41.05; H, 4.49%. ^{1}H NMR ($CDCl_3$): δ9.1 (s,br, OH), 3.14 (vt, OCH_3, $J^3 + J^5$ (P–H) = 12Hz), 7.54 (m, H-ring), 2.60 (d,br,CH_2)ppm. Λ_M (acetone): 128.2 ohm^{-1}mol^{-1}cm^2.

$[(dppe)Pd\{P(O)(OEt)_2\}_2H]ClO_4$, (VII): Yield 286 (76%). Anal.: Calcd. for $C_{34}H_{45}ClO_{10}P_4Pd$: C, 46.43; H, 5.56%. Found: C, 46.14, H, 5.14%. ^{1}H NMR ($CDCl_3$) : δ3.79 (m,CH_2,OEt), 0.96 (t,CH_3,OEt, ^{3}J(H–H) = 7Hz), 7.68 (m, H-ring) ppm, CH_2 (dppe) no resolved. Λ_M (acetone): 114.8 ohm^{-1}mol^{-1}cm^2.

$[(bipy)Pd\{P(O)(OMe)_2\}_2H]PF_6$ (VIII): Yield 178 mg (71%). Anal.: Calcd. for $C_{14}H_{21}F_6N_2O_6P_3Pd$: C, 28.63; H, 3.38; N, 4.47%. Found: C, 26.72; H, 3.37; N, 4.60%. ^{1}H NMR ($CDCl_3$): δ13.8 (s,br, OH), 3.88 (vt,OCH_3, $J^3 + J^5$(P–H) = 12Hz), 7.6–9.0 (m, H-ring) ppm. Λ_M (acetone) : 131.0 ohm^{-1}mol^{-1}cm^2.

$[(bipy)Pd\{P(O)(OEt_2\}_2H]ClO_4$ (IX): Yield 219 mg (80%). Anal.: Calcd. for $C_{18}H_{29}ClN_2O_{10}P_2Pd$: C, 33.93; H, 4.59; N, 4.40% Found: C, 34.00; H, 4.66; N, 4.36%. ^{1}H NMR ($CDCl_3$): δ4.30 (m,CH_2), 1.40 (t,CH_3, ^{3}J(H–H) = 7Hz), 7.8–9.0 (m, H-ring) ppm. Λ_M (acetone): 127.7 ohm^{-1}mol^{-1}cm^2.

$[(Et_3P)ClPd\{P(O)(OMe)_2\}_2Rh(COD)]$ (X)

To a solution of $[(Et_3P)ClPd\{P(O)(OMe)_2\}_2H]$ (143.7 mg; 0.3 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of the dimer complex $[Rh(OMe)(COD)]_2$[11] (76.6 mg; 0.15 mmol) in CH_2Cl_2. The yellow solution obtained was stirred for 1 h and then concentrated *in vacuo* to a small volume. Careful addition of *n*-pentane gave a yellow-orange solid. Yield 45 mg (22%). Anal.: Calcd. for $C_{18}H_{39}ClO_6P_3PdRh$: C, 31.37; H, 5.70%. Found: C, 31.09; H, 5.52%.

$[(dppe)Pd\{P(O)(OMe)_2\}_2Rh(COD)]PF_6$ (XI)

A solution of $[(dppe)Pd\{P(O)(OMe)_2\}_2H]PF_6$ (173.8 mg; 0.2 mmol) in CH_2Cl_2 (10 cm^3) was treated with $[Rh(OMe)(COD)]_2$ (48.4 mg; 0.1 mmol). The mixture was stirred for 1 h and vacuum evaporated to dryness. The residue was extracted with acetone and the slow addition of diethyl ether led to the precipitation of a yellow solid which was filtered off, washed with diethyl ether, and vacuum dried. Yield 122 mg (57%). Anal.: Calcd. for $C_{38}H_{48}O_6P_4PdRh$: C, 40.63; H, 4.38%. Found: C, 40.54, H, 4.43%.

Pd{(μ-Cl)(μ-P(O)(OEt)$_2$)Rh(COD)}$_2$(XII)

A suspension of [Rh(OMe)(COD)]$_2$ (291 mg; 0.60 mmol) and [PdCl{P(O)(OEt)$_2$}$_2$H]$_2$ (501 mg; 0.60 mmol) in MeOH (10 cm^3) was stirred at room temperature for 6 h. The yellow orange solid which formed was filtered off and washed with methanol. The mother liquor was chromatographed on Kieselgel (HF$_{254}$, type 60) using dichloromethane as eluent, the yellow solution obtained was concentrated and a second crop of complex was crystallized by cooling. Yield 405 mg (77%). Anal.: Calcd. for $C_{24}H_{44}Cl_2O_6P_2PdRh_2$: C, 32.99; H, 5.08%. Found: C, 32.92; H, 5.45%.

Pd{(μ-Cl)(μ-P(O)(OR)$_2$)Rh(CO)PPh$_3$}$_2$ (R = Me (XIII), Et (XIV)

The bubbling of carbon monoxide through a CH_2Cl_2 solution of Pd{(μ-Cl)-(μ-P(O)(OR)$_2$)Rh(COD)}$_2$ (0.25 mmol) at room temperature for 15 min caused a displacement of COD. To the resulting solution, containing the carbonyl derivative, was added dropwise the stoichiometric amount of PPh$_3$ in dichloromethane solution. The mixture was stirred at room temperature for 2 h. The complex with R = Et was isolated by partial evaporation and addition of petroleum ether. For the R = Me complex, partial evaporation gave a small quantity of a solid, identified as [RhCl(CO)(PPh$_3$)$_2$]. The solution was chromatographed on Kieselgel using dichloromethane as eluent and the trinuclear complex was crystallized by adding petroleum ether.

XIII: Yield 115 mg (40%). Anal.: Calcd. for $C_{42}H_{42}Cl_2O_8P_2PdRh_2$: C, 42.68; H, 3.58%. Found: C, 42.94; H, 3.42%. ^{1}H NMR (CDCl$_3$): δ3.20 (vt,CH$_3$,$J^3 + J^5$ (P–H) = 14Hz), 7.72, 7.42 (m,H-ring) ppm.

XIV: Yield 102 mg (33%). Anal.: Calcd. for $C_{46}H_{50}Cl_2O_8P_2PdRh_2$:C, 44.63; H, 4.01%. Found: C, 44.91; H, 3.87%. ^{1}H NMR (CDCl$_3$): δ3.50 (m,CH$_2$), 1.22 (t,CH$_3$, ^{3}J(H–H) = 7Hz), 7.76, 7.42 (m, H-ring) ppm.

RESULTS AND DISCUSSION

Mononuclear complexes

The binuclear palladium(II) complex [PdCl{P(O)(OR)$_2$}$_2$H]$_2$ (R = Me, Et) reacts with the stoichiometric amount of the phosphine ligands PR$'_3$ (R′ = Et, Ph), in dichloromethane solution by cleavage of the chlorine bridges to yield neutral complexes, according to equation (*1*)

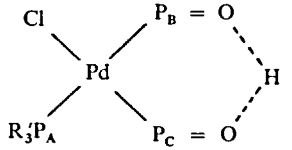
$$[PdCl\{P(O)(OR)_2\}_2H]_2 + 2PR'_3 \longrightarrow 2[(PR'_3)ClPd\{P(O)(OR)_2\}_2H] \qquad (1)$$

I: R = Me, R′ = Et; II: R = Et, R′ = Et; III: R = Me, R′ = Ph; IV: R = Et, R′ = Ph.

These compounds were isolated as stable microcrystalline white solids. Their ^{1}H NMR spectra in deuterated chloroform show the expected two OR signals indicated non-equivalent phosphonate groups, a broad singlet at low field corresponding to the acidic proton (POH), and the characteristic resonances of the phosphine ligand.

The proton-decoupled ^{31}P NMR spectra of the complexes I-IV show a doublet of doublets for the PR$'_3$ ligand, a doublet of doublets for the P(O)(OR)$_2$ ligand bonded *trans* to PR$'_3$ with a large phosphorus–phosphorus coupling, and a doublet of doublet or triplets for the *cis* (to PR$_3'$) bonded phosphonate. The triplet signal that appears for the *cis* P(O)(OR)$_2$ ligands in complexes I and IV is due to the overlap of signals resulting from the similar values of both *cis* phosphorus–phosphorus coupling.[5,12] The assignments are collected in Table I.

TABLE I
^{31}P{^{1}H} NMR spectral data for the complexes.[a]



Complex	δP(O)(OR)$_2$	J(P–P)Hz	δP$_A$R$_3'$
I	100.90 dd(P$_B$) 81.07 t(P$_C$)	P$_A$–P$_B$ = 590.30 P$_A$–P$_C$ = 9.60 P$_B$–P$_C$ = 7.40	22.50 dd
II	98.64 dd(P$_B$) 77.47 dd(P$_C$)	P$_A$–P$_B$ = 585.00 P$_A$–P$_C$ = 10.42 P$_B$–P$_C$ = 2.89	19.20 dd
III	94.06 dd(P$_B$) 80.11 dd(P$_C$)	P$_A$–P$_B$ = 604.00 P$_A$–P$_C$ = 15.00 P$_B$–P$_C$ = 6.00	24.00 dd
IV	91.50 dd(P$_B$) 76.96 t(P$_C$)	P$_A$–P$_B$ = 599.93 P$_A$–P$_C$ = 14.89 P$_B$–P$_C$ = 10.42	22.32 dd

[a] Chemical shifts are in ppm relative to 85% H_3PO_4.

Attempts to obtain cationic palladium complexes of the type [L$_2$Pd{P(O)-(OR(2}$_2$H]$^+$, where L$_2$ is the bidentate ligand 2,2-bipyridine (bipy) or 1,2-bis-(diphenylphosphino)ethane (dppe), by direct reaction of the binuclear starting complexes with the bidentate ligands were unsuccessful. Thus, the reaction of [PdCl{P(O)(OMe)$_2$}$_2$H]$_2$ with bipy or dppe in dichloromethane solution gives a mixture of uncharacterized mononuclear complexes. However, a similar reaction with [PdCl}P(O)(OEt)$_2$}$_2$H]$_2$ shows that the bidentate ligand cleaves the chlorine bridge and displaces the dialkylphosphite group, forming the mononuclear neutral complex L$_2$PdCl{P(O)(OEt)$_2$}. The complex with L$_2$ = bipy (V) was fully characterized and the ^{1}H NMR spectrum shows a triplet signal at δ1.40 ppm (CH$_3$, 6H, ^{3}J(H–H) = 7Hz) and a multiplet at 4.30 ppm (CH$_2$, 4H). The ring protons of bipy give rise to three multiplets at 7.6, 8.2 and 9.3 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ39.59 ppm.

When the binuclear starting complexes [PdCl{P(O)(OR)$_2$}$_2$H]$_2$ react with silver salts containing bulky anions in acetone solution intermediate solvate species are formed. The subsequent addition of the bidentate ligands bipy or dppe to the solution led to the formation of cationic complexes, according to (*2*).

$$\tfrac{1}{2}[PdCl\{P(O)(OR)_2\}_2H]_2 + L_2 \xrightarrow[Me_2CO]{AgA} [L_2Pd\{P(O)(OR)_2\}_2H]A + AgCl \qquad (2)$$

VI : L_2 = dppe, R = Me, A = PF_6^-; VII : L_2 = dppe, R = Et, A = ClO_4^-; VIII : L_2 = bipy, R = Me, A = PF_6^-; IX : L_2 = bipy, R = Et; A = ClO_4^-.

The complexes were isolated as stable microcrystalline white solids and behaved as 1 : 1 electrolytes in acetone solution. The solid state infrared spectra show the presence of the uncoordinated anion (PF_6^-: *ca* 840 and 560 cm^{-1}; ClO_4^-: *ca* 1100 and 620 cm^{-1}).

The ^1H NMR spectra of the complexes VI and VIII show the characteristic virtual triplet signal assigned to the methyl of the phosphonate ligands,[13-15] and a broad signal for the acidic proton. The complexes VII and IX show the expected triplet and multiplet signals corresponding to the ethyl groups.

The $^{31}P\{^1H\}$ NMR spectra of the dppe derivatives show two broad doublets with a large *trans* phosphorus–phosphorus coupling, VI: δ91.46 (d,br,$P(O)(OMe)_2$) and 51.64 ppm (d,br,dppe), ^2J(P *trans* P) = 478.50 Hz; VII: δ89.29 (d,br,$P(O)(OEt)_2$) and 45.59 ppm (d,br,dppe), ^2J(P *trans* P) = 479.35 Hz. The spectra of the bipy derivatives give only a single signal, VIII: δ75.99 and IX: δ75.20 ppm.

Heterometallic complexes

The reaction of the neutral mononuclear complex I with the stoichiometric amount of the complex $[Rh(OMe)(COD)]_2$ yields the expected heterometallic complex $[(Et_3P)ClPd\{P(O)(OMe)_2\}_2Rh(COD)]$ (X) as a yellow moisture-sensitive solid, where the anionic form of the complex I is acting as an (O,O) donor ligand. The ^1H NMR spectrum shows the phosphonate methyl resonances at δ3.71 ppm (vt,OCH_3, $J^3 + J^5$(P–H) = 12 Hz) and the signals of the ancillary ligands (Et_3P: δ1.2 (m,CH_3), 2.0 ppm (m,CH_2); COD: δ1.8 (m,CH_2, 2.5 (m,CH_2), 4.16 ppm (s,br,CH = CH).

In contrast, when the reaction was performed with the PPh_3 derivatives III or IV, the evaporation of solvent led to a solid mixture of the previously described complexes $[(Ph_3P)ClRh(COD)]$[10] and $[Pd\{P(O)(OR)_2\}_2]_n$.[9]

Similarly, the cationic complex VI, $[(dppe)Pd\{P(O)(OMe)_2\}_2H]PF_6$, reacts with the stoichiometric amount of $[Rh(OMe)(COD)]_2$ to give the heterometallic cationic complex $[(dppe)Pd\{P(O)(OMe)_2\}_2Rh(COD)]PF_6$ (XI). Its ^1H NMR spectrum shows the corresponding virtual triplet for the methyl group (δ3.14 ppm, $J^3 + J^5$(P–H) = 12 Hz) and signals of the bidentate ligands (COD: δ1.26 (m,CH_3), 2.60 (m,CH_2), 3.87 ppm (s,br,CH=CH); dppe: δ2.60 (m,CH_2, masked by COD), 7.63 ppm (m,H-ring)). The $^{31}P\{^1H\}$NMR spectrum shows two doublets at δ91.60 and 52.26 ppm, assigned to phosphonate and dppe ligands respectively, with a *trans* phosphorus–phosphorus coupling of 509.5 Hz. The analogous reaction performed with the bipy derivatives VIII or IX gives different results, possibly due to the lability of the bipy-Pd(II) bond. In fact, all attempts at synthesis show a migration of the bipy ligand from the palladium(II) to the rhodium(I) metal centre, to yield the mononuclear cationic complex [(bipy)Rh(COD)]A (A = PF_6^-, ClO_4^-). Similar results were obtained when the reaction was carried out with the complexes $[PdCl(\eta^3\text{-}MeC_3H_4)]_2$[16] or $[Cu(OMe)(acac)]_2$,[19] yielding $[(bipy)Pd(\eta^3\text{-}MeC_3H_4)]A$ or [(bipy)-Cu(acac)]A complexes respectively, together with corresponding polymeric palladium(II) complex $[Pd\{P(O)(OR)_2\}_2]_n$. The products of the above reactions were characterized mainly by comparison of their IR and ^1H NMR spectra with pure samples obtained by reported methods.[18-20].

On the other hand, reaction of $[PdCl\{P(O)(OEt)_2\}_2H]_2$ with an equimolecular amount of $[Rh(OMe)(COD)]_2$ in methanol suspension gives a yellow-orange solid characterized as the heterotrinuclear complex $Pd\{(\mu Cl)(\mu\text{-}P(O)(OEt)_2)Rh(COD)\}_2$ (XII). The ^1H NMR spectrum shows the signals of the ethyl group (δ1.34(t,CH_3, $^3J(H\text{-}H) = 7$ Hz), 4.18 ppm (m,CH_2)), and the coordinated COD (δ1.72 (m,CH_2), 2.42 (m,CH_2), 4.18 ppm (CH=CH) masked by the ethyl signal) in the required intensity ratios, supporting the proposed formulation. The $^{31}P\{H\}$ NMR spectrum shows a singlet at δ90.76 ppm. The structure of this complex is probably similar to that determined by X-ray diffraction for the related complex containing dimethylphosphonate as ligand, in which two Rh(COD) fragments are bridged by a pair of identical Cl/P=O groups to both sides of a square planar palladium atom.[8]

The bubbling of carbon monoxide through a dichloromethane solution of complex XII caused the displacement of the coordinated diolefin COD and the formation of the tetracarbonyl derivative $Pd\{\mu\text{-}Cl)(\mu\text{-}P(O)(OEt)_2)Rh(CO)_2\}_2$. The infrared spectrum of the solution shows strong ν(CO) adsorption at 2010 and 2090 cm^{-1}, characteristic of a *cis* arrangement of the carbonyl groups. The carbonylation of the previously described complex $Pd\{(\mu\text{-}Cl)(\mu\text{-}P(O)(OMe)_2)Rh(COD)\}_2$ shows similar results,[8] giving two ν(CO) bands at 2010 and 2085 cm^{-1} (CH_2Cl_2). This fact confirms that both complexes have a similar structure.

Unfortunately, the tetracarbonlyl complexes could not be isolated in the solid state as pure samples. However, the additon of PPh_3 to the dichloromethane tetracarbonyl solutions in a 2 : 1 molar ratio, led to evolution of carbon monoxide with formation of the stable dicarbonyl derivatives $Pd\{(\mu\text{-}Cl)(\mu\text{-}P(O)(OR)_2)Rh(CO)PPh_3\}_2$ (R = Me (XIII); Et (XIV)). These complexes show only a single broad band in the carbonyl IR region, XIII: 1940 cm^{-1} (CH_2Cl_2), 1960 cm^{-1} (KBr); XIV: 1940 cm^{-1} (CH_2Cl_2), 1955 cm^{-1} (KBr). The addition of excess PPh_3 led to cleavage of the bridges and to formation of the mononuclear complex $[RhCl(CO)(PPh_3)_2]$.[21]

ACKNOWLEDGEMENTS

One of us (M.V.) wishes to thank Professors Rafael Usón and Luis A. Oro (Universidad de Zaragoza) for laboratory facilities and to the Spanish Sabbatical Program for a grant. This work was also partially supported by the Dirección de Investigación, Pontificia Universidad Católica de Chile (DIUC) and the Stiftung Volkswagenwerk.

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