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The First Palladium(0) Complex with Only Secondary Phosphines as Ligands and Its Oxidative-Addition Reactions with CH_2Cl_2 and $CHCl_3$, Giving the Thermally Stable Derivatives *trans*-$[PdCl(R)(PBu^t_2H)_2]$ (R = CH_2Cl, $CHCl_2$)

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Summary: $Pd(PBu^t_2H)_3$, *(1), obtained by reacting* $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ *with* PBu^t_2H, *oxidatively adds the C–Cl bond of methylene chloride and of chloroform, giving the thermally stable derivatives trans-*$[PdCl(CH_2Cl)(PBu^t_2H)_2]$, *(2) and trans-*$[PdCl(CHCl_2)(PBu^t_2H)_2]$, *(3), respectively. Complex 1 solutions deposit, by gentle warming, the known dimer* $[Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)]_2$.

Although tertiary phosphines are ubiquitous ligands in coordination and organometallic chemistry,[1] the amount of data available on primary and secondary phosphine metal complexes are relatively scarce. Notably low is the number of reports on the synthesis of low-valent mononuclear complexes with late transition metals. Only two types of d^7 systems appear to have been reported, namely $[IrH(PEt_2H)_5]Y$[2] and $CoX_2(PR_2H)_n$;[3] something more is known about d^8 systems (Fe(0),[4,5] Rh(I),[2,6-9] Ir(I),[2,5-9] Ni(II),[10] Pd(II),[7,11] and Pt(II)[12]), and far as d^{10} systems are concerned, examples are limited to Au(I),[13,14] but M(0) partners (M = Ni, Pd, Pt) are unknown. The main obstacle to the isolation of such systems comes from the reactivity of P–H bonds, which easily undergo oxidative addition to electron-rich metal fragments, giving phosphido–hydrido deratives.[6,15] On the other hand, the great aptitude of phosphido ligands to bind to late transition metals in a bridging rather than a terminal fashion accounts for the utility of secondary phosphine complexes as precursors to polynuclear derivatives.[16]

An earlier report[17] on the reactivity of $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ with PBu^t_2H described the formation of the Pd(I) dimer $[Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)]_2$. The reaction proceeds in high yield under severe thermal conditions, and the dimer was suggested to form through the intermediacy of $Pd(PBu^t_2H)_2$. Interest in such a compound as a promising building block for the synthesis of new mono- and polynuclear Pd derivatives stimulated a reexamination of the reaction.

$Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ reacts rapidly and completely with PBu^t_2H in excess, giving a colorless, air-sensitive solid (92% yield) which has been characterized by spectroscopic and elemental analyses as $Pd(PBu^t_2H)_3$ (**1a**).[18] The IR spectrum of **1a** exhibits a single ν_{PH} band of medium-strong intensity at 2244 cm^{-1}, while $\nu_{=CH}$ bands in the 3100–3000-cm^{-1} region are missing. The absence of both the Cp and allyl functionalities[19] has been confirmed by NMR spectroscopy (benzene-d_6, 293 K). The ^1H NMR spectrum consists of two slightly broadened doublets (integrated ratio 1:18), one at 4.40 ppm with a typical large $^1J_{PH}$ value (256 Hz) for the P–H protons and the second at 1.42 ppm ($^3J_{PH}$ = 27 Hz) for the *tert*-butyl protons. The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8, 293 K) shows a singlet at 54.5 ppm that splits into a broadened doublet ($^1J_{PH}$ = 256 Hz) in the corresponding proton-coupled spectrum. ^1H and proton-coupled ^{31}P NMR spectra of $M(PR_2H)_n$ fragments ($n > 1$) are generally more complicated due to the presence of the $[AMX_m]_n$ spin system (A = *P*, M = P–*H*, X = R protons);[10a,11a,20] the simplicity of complex 1 spectra suggests a rapid equilibration (eq 1) causing the loss of PP′, PH′, and HH′ inter-phosphine couplings.

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(18) $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ (807 mg, 4.09 mmol) was dissolved in acetone (15 mL) and slowly dropped at 0 °C into a solution of 2.442 g (16.7 mmol) of PBu^t_2H in acetone (10 mL). A colorless solid precipitated during the addition. The mixture was stirred for 15 min at room temperature, and the solid was filtered, washed with acetone (10 mL), and *vacuum* dried, giving 2.05 g of **1a**. Anal. Calcd for $C_{24}H_{57}P_3Pd$: C, 52.9; H, 10.5. Found: C, 52.4; H, 10.2.

(19) (a) The formation of complex 1 is accompanied by the reductive elimination of 5-allyl-1,3-cyclopentadiene, which rapidly isomerizes to 1-allyl-1,3-cyclopentadiene (^{13}C NMR (C_6D_6, 293 K) δ 147.08 (147.43) s, 137.28 (137.42) d, 132.77 (132.57) d, 131.11 (131.02) d, 127.34 (127.50) d, 115.42 (115.00) t, 43.34 (43.30) t, 35.54 (35.49) t)[19b] and then, slowly, to an equilibrium mixture of 1- and 2-allyl-1,3-cyclopentadiene (^{13}C NMR C_6D_6, 293 K) δ 145.03 (145.24) s, 136.67 (136.77) d, 134.89 (134.77) d, 133.80 (133.71) d, 126.98 (126.85) d, 115.73 (115.25) t, 41.45 (41.37) t, 34.24 (34.63) t].[19b] The same behavior was observed in the reaction of $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ with tertiary phosphines.[19c,d] (b) Literature δ values (in parentheses) taken from: Hill, E. A.; Hsieh, K.; Condroski, K.; Sonnentag, H.; Skalitzky, D.; Gagas, D. *J. Org. Chem.* **1989,** *54,* 5286. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 1. (d) Parker, G.; Werner, H. *Helv. Chim. Acta* **1973,** *56,* 2819.

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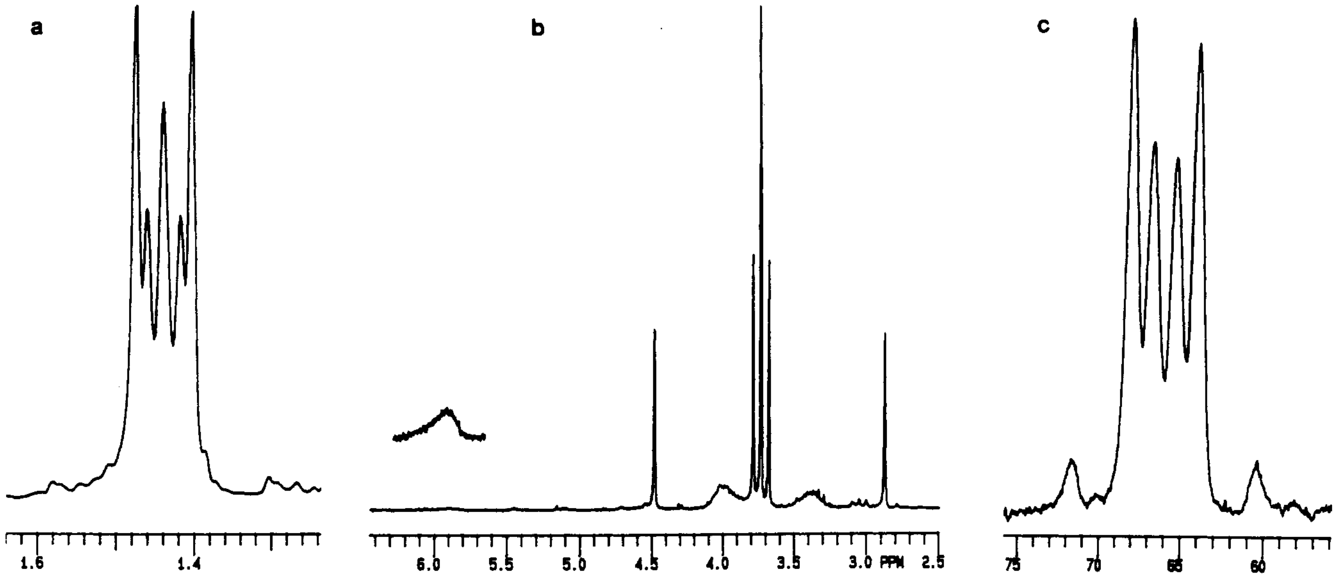

Figure 1. NMR spectra of complex **2**, showing the subspectra of the $[AMX_{18}]_2$ spin system: (a) ^1H spectrum, X component ($C(CH_3)_3$ protons); (b) ^1H spectrum, M component (P–H protons) and the CH_2Cl triplet; (c) proton-coupled ^{31}P spectrum, A component.

$$\underset{\textbf{1a}}{Pd(PBu^t_2H)_3} \rightleftarrows \underset{\textbf{1b}}{Pd(PBu^t_2H)_2} + PBu^t_2H \qquad (1)$$

The above equilibrium was confirmed by low-temperature $^{31}P\{^1H\}$ NMR spectra (toluene-d_8). At 203 K the main singlet is found at 55.1 ppm and new small singlets appear at 62.1 and 17.5 ppm; the signal at 17.5 ppm has been assigned to free PBu^t_2H, by comparison with a sample of the pure ligand analyzed under identical conditions (toluene-d_8, 203 K).[21] The signals at 55.1 and 62.1 ppm have been attributed to **1a** and **1b**, respectively. Although quantitative comparisons of peak areas are affected by large errors in $^{31}P\{^1H\}$ NMR spectroscopy, **1a** was qualitatively observed to be the predominant species in solution.[22] Addition of excess PBu^t_2H did not affect significantly the chemical shift of the signal at 55.1 ppm or the yields or the elemental analyses of the preparations, suggesting that $Pd(PBu^t_2H)_4$ is not accessible for steric reasons.

As far as its reactivity is concerned, at least two sites in complex **1a** are susceptible to profitable synthetic manipulations: (a) the P–H bonds of the secondary phosphines, which can oxidatively add to other metal fragments and generate new polynuclear derivatives, and (b) the electron-rich metal, to which a reactivity pattern similar to that observed in the parent Pd(0) tertiary phosphine complexes[23] can in principle be ascribed. The previously anticipated[17] intermediacy of a Pd(0) PBu^t_2H complex in the formation of the Pd(I) dimer $[Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)]_2$ was confirmed; in fact, gentle warming of a toluene solution of **1a** causes the dimer to quantitatively separate out with H_2 evolution.

The Pd center easily undergoes oxidative-addition reactions. Complex **1a** was suspended in CH_2Cl_2 and stirred at ambient temperature. Complete dissolution of the solid was observed in a few minutes and, after workup, 70% of pure *trans*-$[PdCl(CH_2Cl)(PBu^t_2H)_2]$ (**2**) was obtained as a colorless, microcrystalline solid which was characterized by means of spectroscopic and elemental analyses.[24]

The IR spectrum of complex **2** shows ν_{PH} at 2332 cm^{-1}; ν(as) and ν(s) for the CH_2 function were observed at 2979 and 2943 cm^{-1}, respectively, and shifted to 2239 and 2156 cm^{-1} in the CD_2 analogue. The presence of the chloromethyl functionality was confirmed by ^1H NMR spectra (benzene-d_6, 293 K), which exhibit a sharp triplet ($^3J_{PH}$ = 10.9 Hz) at 3.73 ppm, typical of CH_2X protons coupled to two equivalent phosphines (*trans*-$[PdCl(CH_2Cl)(PCy_3)_2]$ δ 3.92 ppm, t, $^3J_{PH}$ = 8.0 Hz);[25] this signal was absent when CD_2Cl_2 was used instead of CH_2Cl_2. The two chemically equivalent but magnetically inequivalent phosphine ligands produce the expected $[AMX_{18}]_2$ patterns (A = P, M = P–H, X = $C(CH_3)_3$) in the ^1H and proton-coupled ^{31}P NMR spectra.[10a,11a,20] The ^1H NMR spectrum shows the X part of the spin system, constituted by the approximately 2:1:2:1:2 quintet at 1.44 ppm (Figure 1a) due to the *tert*-butyl protons;[20] other signals in the spectrum are a sharp doublet ($^1J_{PH} + {}^3J_{PH_M}$ = 321.8 Hz) and a broad doublet ($J_{apparent}$ = 125 Hz) both centered at 3.68 ppm (Figure 1b) which constitute part of the M subspectrum (only the low-field element of a third symmetrical broad doublet was observed, the upfield element being hindered under the *tert*-butyl signal; $J_{apparent}$ and the intensity of this doublet depend on $^2J_{PP}$).[10a,11a,20] $^{31}P\{^1H\}$ spectra show a sharp singlet at 65.9 ppm, which splits into a six-line signal (Figure 1c) in

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[21] $^{31}P\{^1H\}$ NMR chemical shifts of phosphines are temperature dependent; $\Delta\delta/\Delta T$ values in the range 0.002–0.07 ppm/deg have been measured in: Gordon, M. D.; Quin, L. D. *J. Magn. Reson.* **1976**, *22*, 149. $^tBu_2PH$ absorbs at 20.2 ppm at 293 K.

[22] The amount of dissociation of **1a** at 203 K is ca. 5–10%, as evaluated by integration of $^{31}P\{^1H\}$ NMR spectra. However, meaningful comparison of peak areas of ^{31}P NMR spectra is only obtainable in proton-coupled spectra (to avoid NOE effects). Moreover, free phosphines have long relaxation times, and long delays between each pulse should be employed. For both of these effects, and for the low solubility of the complex at 203 K, the time necessary to acquire spectra with correct integral ratios becomes prohibitively long. ^1H NMR was not practical for this purpose because of serious overlapping of the signals.

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the corresponding proton-coupled spectrum (part A of the spin system).[10a,11a] $^1J_{PH} = 318$, $^2J_{PP} = 380$, $^3J_{PH_M} = 3.75$, $^3J_{PH_X} = 13.9$, and $^5J_{PH_X} < 1$ Hz could be extracted directly from the spectra, as indicated in the literature, and were consistent with the values for the analogue *trans*-$[MXY(PR_2H)_2]$.[10a,11a,20]

The same kind of reactivity was observed with $CHCl_3$, and *trans*-$[PdCl(CHCl_2)(PBu^t{}_2H)_2]$ (**3**) was isolated in 65% yield. The dichloromethyl ligand was observed at $\delta_H = 6.15$ ppm (t, $^3J_{PH} = 11.2$ Hz, missing in the $CDCl_2$ analogue); all other signals in ^1H, $^{31}P\{^1H\}$, and ^{31}P NMR spectra were consistent with the suggested structure[26] and much similar to the corresponding signals in the spectra of complex **2**.

Thermal[25,27] and photochemical[25,28,29] CH_2Cl_2 activation has precedents; however, undesired bimolecular decomposition of the chloromethyl derivatives to the corresponding chlorides and ethylene has often been observed. Similar decomposition pathways are even more accessible to dichloromethyl derivatives, which have been rarely observed as transient species and occasionally isolated.[27f,29] Complexes **2** and **3** are stable both in the solid state and in solution[30] and represent excellent starting materials for the synthesis of a large variety of palladium organometallics[31] and good candidates for studies of catalytic incorporation of CH_2Cl_2 and $CHCl_3$ in organic chemicals by C–C-bond-forming cross-coupling reactions.[32]

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(26) Anal. Calcd for $C_{17}H_{39}Cl_3P_2Pd$: C, 39.4; H, 7.59. Found: C, 39.1; H, 7.65. ^1H NMR (C_6D_6, 293 K): δ 6.15 (1 H, t, $^3J_{PH} = 11.2$ Hz, C*H*Cl_2), 3.81 (M part of the $[AMX_{18}]_2$ spin system, 2 H, P–*H*), 1.50 (X part of the $[AMX_{18}]_2$ spin system, 36 H). $^{31}P\{^1H\}$ NMR: δ 62.22 s. ^{31}P NMR: δ 62.22 (A part of the $[AMX_{18}]_2$ spin system); $^1J_{PH} = 318$, $^2J_{PP} = 387$, $^3J_{PH_M} = 11$, $^3J_{PH_X} = 14.1$, and $^5J_{PH_X} < 1$ Hz from ^1H and ^{31}P spectra.[21]

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