Bull Soc Chim Fr (1996) 133, 669-672

Communication

Ligand redistribution reactions leading to new phosphinoenolate, methyl palladium complexes. Crystal structure of [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)]†

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(Received 25 January 1996; accepted 21 May 1996)

Summary — Phosphinoenolate, methyl palladium(II) complexes were prepared in high yields by a sequence of reactions involving phosphine redistribution reactions. Thus, reaction of the dinuclear complex [Pd(Me)(μ-Cl){$Ph_2PCH_2C(O)NPh_2$}]$_2$ **1** with PCy_3 in CH_2Cl_2 led to a mixture of [Pd(Me)Cl(PCy_3){$Ph_2PCH_2C(O)NPh_2$}] **2**, *trans*-[Pd(Me)Cl(PCy_3)$_2$] **3** and *trans*-[Pd(Me)Cl{$Ph_2PCH_2C(O)NPh_2$}] **4**. However, reaction of this mixture with NaOMe in toluene afforded selectively [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph_2$}($PCy_3$)] **5**. This procedure was extended to the ketophosphinoenolate complexes [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PCy_3$)] **7** and [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)] **8**. Based on the ligand redistributions observed, a high-yield one-pot synthesis of **5**, **7** and **8** is described. The crystal structure of **8** was determined by X-ray diffraction.

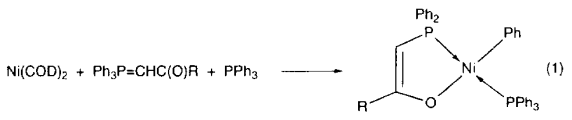
alkyl complex / phosphinoenolate complex / redistribution reaction / palladium

Résumé — Réactions de redistribution de ligands conduisant à de nouveaux complexes méthyl phosphinoénolates du palladium. Structure cristalline de [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)]. *Des complexes méthyl, phosphinoénolate du palladium(II) ont été obtenus avec de bons rendements par une séquence de réactions impliquant des réactions de redistribution de phosphines. Si le complexe dinucléaire [Pd(Me)(μ-Cl){$Ph_2PCH_2C(O)NPh_2$}]$_2$ **1** réagit avec PCy_3 dans CH_2Cl_2 pour donner [Pd(Me)Cl(PCy_3){$Ph_2PCH_2C(O)NPh_2$}] **2**,* trans-*[Pd(Me)Cl(PCy_3)$_2$] **3** et* trans-*[Pd(Me)Cl{$Ph_2PCH_2C(O)NPh_2$}] **4**, la réaction de ce mélange avec NaOMe dans le toluène conduit sélectivement à [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph_2$}($PCy_3$)] **5**. Cette méthode a été étendue aux complexes phosphinoénolates [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PCy_3$)] **7** et [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)] **8**. Une synthèse «one-pot» à haut rendement de **5**, **7** et **8** est basée sur les réactions de redistribution observées. La structure de ce dernier a été déterminée par diffraction des rayons X.*

complexe alkyle / phosphinoénolate / réaction de redistribution / palladium

Introduction

Phosphinoenolate Ni(II) complexes of the type [Ni(Ph){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)] are considered to be valuable models for the catalysts used in the Shell higher olefin process (SHOP) which converts ethylene into linear α-olefins [1]. Their synthesis is readily performed by oxidative addition of a functional phosphorane to the nickel(0) complex [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) (eq 1).



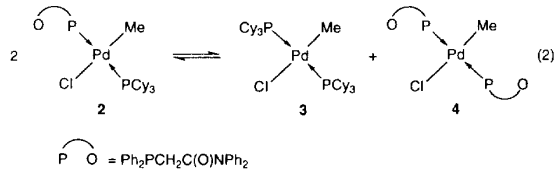
This synthetic procedure is however limited to nickel(0). We were interested in studying the chemistry

† Dedicated to Prof Raymond Weiss.

* Correspondence and reprints

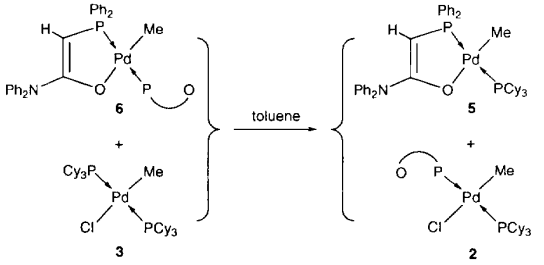
of analogous d^8 metal complexes, particularly of palladium, in view of the numerous applications of this metal in homogeneous catalysis [2]. Since the Pd(0) complexes $Pd(PPh_3)_4$ or $Pd(dba)_2$ did not lead to an oxidative-addition product with the phosphoranes $Ph_3P{=}CHC(O)Ph$ or $Ph_3P{=}CHC(O)Me$, we devised a different synthetic approach based on the synthesis of aryl or alkyl palladium(II) complexes containing the functional phosphines $Ph_2PCH_2C(O)R$ and the deprotonation of their PCH_2 group to give the corresponding phosphinoenolate complexes. Thus, the first palladium analogues of the model SHOP-type nickel catalysts became available [3]. In order to fine-tune the reactivity and catalytic properties of such complexes, it is necessary to be able to vary the ligands and we report here our results on the synthesis of phosphinoenolate palladium(II) methyl complexes containing different phosphine ligands. Reaction of the dinuclear complex $[Pd(Me)(\mu\text{-}Cl)\{Ph_2PCH_2C(O)NPh_2\}]_2$ **1**, prepared from [Pd(Me)Cl(COD)] and 1 equiv $Ph_2PCH_2C(O)NPh_2$, with tricyclohexylphosphine (PCy_3) was expected to yield $[Pd(Me)Cl(PCy_3)\{Ph_2PCH_2C(O)NPh_2\}]$ **2**. Instead, a mixture of **2**, *trans*-$[Pd(Me)Cl(PCy_3)_2]$ **3** and *trans*-$[Pd(Me)Cl\{Ph_2PCH_2C(O)NPh_2\}]$ **4** was formed and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (eq 2).

Complexes **3** and **4** [3] were prepared independently (from [Pd(Me)Cl(COD)] and 2 equiv phosphine) and their mixing in a 1:1 ratio in CH_2Cl_2 resulted in the same mixture of products ($^{31}P\{^1H\}$ NMR monitoring) which are therefore in thermodynamic equilibrium. Complex **2** is the only complex in this mixture that gives a typical AB pattern in $^{31}P\{^1H\}$ NMR spectroscopy. It cannot be isolated pure owing to the existence of the equilibrium shown in equation 2:



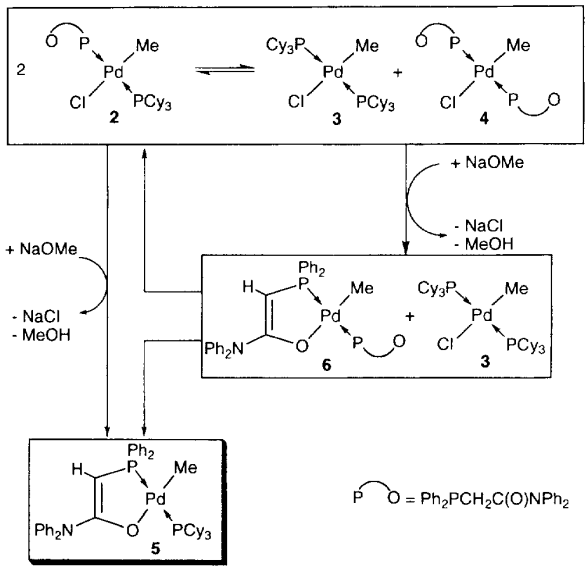
Fortunately, the desired phosphinoenolate complex $[Pd(Me)\{Ph_2PCH{\cdots}C(\cdots O)NPh_2\}(PCy_3)]$ **5** quantitatively formed upon reaction of the equilibrium mixture **2**, **3** and **4** with NaOMe in toluene. Although complex **4** could have led to $[Pd(Me)\{Ph_2PCH{\cdots}C(\cdots O)NPh_2\}\{Ph_2PCH_2C(O)NPh_2\}]$ **6** [3] by reaction with NaOMe, it was not isolated. Again, ligand redistribution reactions are at work, as demonstrated by the following experiment. Complexes **3** and **6** were mixed in a 1:1 ratio in toluene and $^{31}P\{^1H\}$ NMR monitoring indicated the formation of **2** and **5** (scheme 1). In turn, complex **2** will react with NaOMe to give **5**.

An alternative pathway to **5** from the mixture of equation 2 would be the faster deprotonation of **2** compared to **4**, thus shifting the equilibrium towards the left. Although it cannot be ruled out, this appears less likely in view of the basicity of the PCy_3 ligand.



Scheme 1

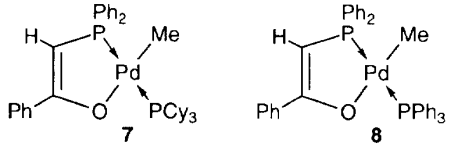
All these possibilities are summarized in scheme 2 and account for the selective formation of **5** from a mixture of phosphine or phosphinoenolate complexes.



Scheme 2

A one-pot synthesis of **5** is therefore achieved by the reaction of [Pd(Me)Cl(COD)] with 1 equiv of $Ph_2PCH_2C(O)NPh_2$ and 1 equiv PCy_3 in CH_2Cl_2, followed by solvent evaporation and addition of a toluene suspension of NaOMe. After stirring overnight, the desired product was isolated in 90% yield.

This procedure was extended to the ketophosphinoenolate complexes $[Pd(Me)\{Ph_2PCH{\cdots}C(\cdots O)Ph\}(PCy_3)]$ **7** and $[Pd(Me)\{Ph_2PCH{\cdots}C(\cdots O)Ph\}(PPh_3)]$ **8**.



A diagram of the molecular structure of **8** is shown in figure 1.

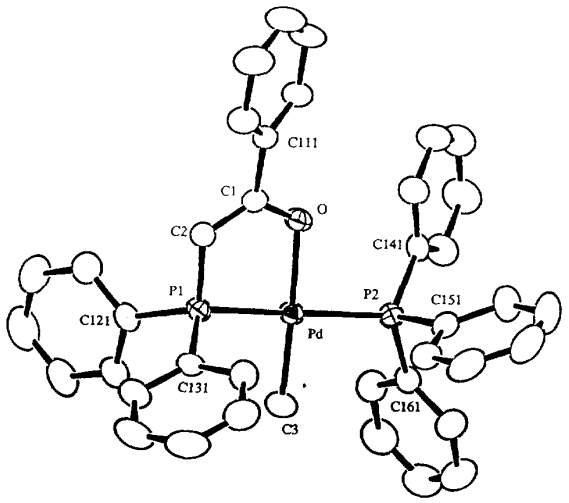


Fig 1. Ortep diagram of the molecule structure of [Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)] **8** showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Pd-P(1) = 2.2708(9), Pd-P(2) = 2.3324(9), Pd-O = 2.119(2), Pd-C(3) = 2.039(3), C(1)-C(2) = 1.368(4), C(1)-O = 1.298(3), P(1)-C(2) = 1.756(3); P(1)-Pd-P(2) = 174.04(3), O-Pd-C(3) = 173.2(1), P(1)-Pd-O = 83.06(6), P(2)-Pd-O = 94.47(6), P(2)-Pd-C(3) = 90.4(1).

The molecule is structurally similar to that of **1** [7]. The coordination about the palladium atom is nearly planar with the phosphorus atoms *trans* to one another, P-Pd-P = 174.04(3)°. The methyl group is *trans* with respect to the harder oxygen atom, as the phenyl group in the related nickel(II) complex **1** used as a model for the SHOP-catalyst, Pd-O = 2.119(2) Å, Pd-C(3) = 2.039(3) Å and O-Pd-C(3) = 173.2(1)°. The dimensions within the five-membered P,O-chelate are similar to those in other Pd(II) complexes previously characterized [8]. In particular, the C(1)-C(2) and C(1)-O bond lengths, 1.368(4) Å and 1.298(3) Å, respectively, are consistent with electronic delocalization within the enolate moiety.

Experimental section

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were purified under nitrogen by conventional methods. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC 300 instrument. IR spectra were recorded in the 4 000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer.

Syntheses

The ligands $Ph_2PCH_2C(O)Ph$ [4] and $Ph_2PCH_2C(O)NPh_2$ [5] and the complex [Pd(Me)Cl(COD)] [6] were prepared according to the literature.

• *[Pd(μ-Cl)(Me){$Ph_2PCH_2C(O)NPh_2$}]$_2$* **1**
Acetone (20 mL) was added to a mixture of [Pd(Me)Cl(COD)] (0.200 g, 0.755 mmol) and $Ph_2PCH_2C(O)NPh_2$ (0.299 g, 0.755 mmol). After being stirred for 3 days, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and filtered. The solution was concentrated to one third of the original volume. Addition of pentane afforded a white powder which was filtered and dried in vacuo (0.375 g, 90%).

IR (KBr): ν(CO) 1 663 cm^{-1} (vs).

^1H NMR ($CDCl_3$): δ 0.57 (d, 3H, CH_3, ^3J(PH) = 2.1 Hz), 3.55 (d, 2H, PCH_2, ^2J(PH) = 9.6 Hz), 7.84–7.13 (m, 40H, aromatic).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.9 (s).

Anal for $C_{54}H_{50}Cl_2N_2O_2P_2Pd_2$ (M = 1104.70) calc C: 58.71, H: 4.56, N: 2.54. Found: C: 58.38, H: 4.54, N: 2.42%.

• trans-*[Pd(Me)Cl(PCy_3)$_2$]* **3**
Compound **3** was prepared in CH_2Cl_2 in a manner similar to **4** [3], using PCy_3 in place of $Ph_2PCH_2C(O)NPh_2$. Selected data:

^1H NMR ($CDCl_3$): δ 0.13 (t, 3H, CH_3, ^3J(PH) = 5.2 Hz).

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.5 (s).

• *'One-pot' synthesis of*
[Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)NPh_2$}($PCy_3$)] **5**
A mixture of 0.670 g (2.53 mmol) [Pd(Cl)Me(COD)], 1.00 g (2.53 mmol) of $Ph_2PCH_2C(O)NPh_2$ and 0.708 g (2.53 mmol) of PCy_3 was stirred in CH_2Cl_2 (40 mL) for 2.5 h and the solvent was evaporated under reduced pressure. To the white solid obtained were added solid NaOMe (0.409 g, 3 equiv) and toluene (40 mL). The mixture was stirred overnight, filtered through Celite and the solvent was evaporated, affording a yellow powder which was dried under vacuum (1.740 g, yield 90%).

^1H NMR (C_6D_6): δ 0.78 (apparent t, 3H, ^3J(PH) = 5.3, CH_3), 1.01–2.05 (m, 33H, Cy), 3.75 (d, 1H, PCH, ^2J(PH) = 5.1 Hz), 6.8–7.85 (20H, aromatic).

$^{31}P\{^1H\}$ NMR (C_6D_6): AB spin system, δ 30.6 (d, $^2J(PP)_{trans}$ = 380 Hz, PCy_3), 16.7 (d, P,O).

Anal for $C_{45}H_{57}NOP_2Pd$ (M = 796.32): calc C: 67.87; H: 7.21; N: 1.76%. Found: C: 65.93; H: 7.68; N: 1.69%.

• *'One-pot' synthesis of*
[Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PCy_3$)] **7**
The procedure was similar to that for **5**, using $Ph_2PCH_2C(O)Ph$ (yield: 92%).

^1H NMR (C_6D_6): δ 0.80 (apparent t, 3H, ^3J(PH) = 5.2 Hz, CH_3), 1.10–2.40 (m, 33H, Cy), 5.10 (d, 1H, PCH, ^2J(PH) = 4.5 Hz), 7.00–8.20 (15H, aromatic).

$^{31}P\{^1H\}$ NMR (C_6D_6): AB spin system, δ 30.6 (d, $^2J(PP)_{trans}$ = 384 Hz, PCy_3), 24.2 (d, P,O).

Anal for $C_{39}H_{52}OP_2Pd$ (M = 705.21): calc: C: 66.42, H: 7.43%. Found: C: 66.30; H: 8.01%.

• *'One-pot' synthesis of*
[Pd(Me){$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PPh_3$)] **8**
The procedure was similar to that for **7**, using PPh_3 (yield: 92%).

IR (KBr): 1 506 s (ν(C$\cdots$C) + ν(C$\cdots$O)).

^1H NMR (C_6D_6): δ 0.70 (dd, 3H, ^3J(PH) = 6.95 and 4.40 Hz, CH_3), 5.15 (d, 1H, PCH, ^2J(PH) = 3.9 Hz), 7.0–8.2 (30H, aromatic).

$^{31}P\{^1H\}$ NMR (C_6D_6): AB spin system, δ 29.2 (d, $^2J(PP)_{trans}$ = 395 Hz, PPh_3), 24.7 (d, P,O).

Anal for $C_{39}H_{34}OP_2Pd$ (M = 687.04); calc C: 68.18, H: 4.99%. Found: C: 67.18; H: 5.11%.

Structural analysis

Single crystals of **8** were obtained from a CH_2Cl_2/pentane solution (1:3). The unit cell and intensity data of **8** were obtained on a Rigaku AFC6S automatic diffractometer at 20 °C using MoK_α radiation: a = 11.708(1) Å, b = 15.523(2) Å, c = 10.555(1) Å, α = 107.07(1)°, β = 114.944(9)°, γ = 74.958(9)°, V = 1642.3(4) Å^3, Z = 2. Data processing was performed on a Digital Equipment Corp. VAX station 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp, The Woodlands, TX. A Lorentz-polarization (Lp) and an empirical absorption correction based on three azimuthal psi scans were applied to the data. Neutral atom scattering factors were calculated by the standard procedures [9a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [9b]. Full matrix least-squares refinements minimized the function: Σ_{hkl} $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. The complex crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated and included in the structure factor calculations, but they were not refined. Final refinement values: 3 787 reflections ($I > 3.0\sigma(I)$), R = 0.025, R_w = 0.31.

Table I. Crystallographic data for the structural analysis of compound [Pd(Me){Ph_2PCH···C(···O)Ph}(PPh_3)] **8**.

Formula	$C_{39}H_{34}OP_2Pd$
Formula weight	687.04
Crystal system	triclinic
Lattice parameters	
a (Å)	11.708(1)
b (Å)	15.523(2)
c (Å)	10.555(1)
α (°)	107.07(1)
β (°)	114.944(9)
γ (°)	74.958(9)
V (Å^3)	1 642.3(4)
Space group	$P\bar{1}$ (#2)
Z	2
ρ_{calc} (g/cm^3)	1.39
μ (Mo K_α) (cm^{-1})	6.92
Temperature (°C)	20
$2\Theta_{max}$ (°)	45.0
No Obs ($I > 3\sigma(I)$)	3 787
No Variables	389
Goodness of Fit	2.15
Max shift in final cycle	0.004
Residuals: R; R_ω	0.025; 0.031
Abs Cor (psi scans)	empirical
Transmission coeff, Max/Min	1.00/0.815
Largest peak in Final Diff Map (e$^-$/Å^3)	0.51

* $R = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||/\Sigma_{hkl}|F_{obs}|$; $R_\omega = [\Sigma_{hkl}\omega(|F_{obs}|-|F_{calc}|^2)/\Sigma_{hkl}\omega F_{obs}^2]^{1/2}$, $\omega = 1/\sigma^2(F_{obs})$; GOF = $[\Sigma_{hkl}(|F_{obs}|-|F_{calc}|/\sigma(F_{obs})]/(n_{data} - n_{vari})$.

Supplementary material

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90426 and is available on request from the Document Supply Center.

Acknowledgments

We are grateful to the Ministère de l'Enseignement Supérieur et de la Recherche and to the CNRS for financial support, to NATO for a research grant (CRG 920073) and to Johnson Matthey PLC for a generous loan of $PdCl_2$.

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b) *Ibid*, Table 2.3.1, pp 149-150.