Synthesis, Characterization, and Reactivity of 1,1′-Bis(diphenylphosphino)osmocene: Palladium(II) Complexes and Their Use as Catalysts in the Methoxycarbonylation of Olefins

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Received October 7, 2002

Summary: The new ligand 1,1′-bis(diphenylphosphino)osmocene (dppo) forms a variety of palladium(II) complexes showing either the κ^2P,P or κ^3Os,P,P bonding mode. The complex [Pd(OTs)(dppo)]OTs (OTs = p-toluenesulfonate) is an effective catalyst precursor for the selective methoxycarbonylation of ethylene to methyl propanoate and of styrene to a mixture of methyl 3-phenylpropanoate and methyl 2-phenylpropanoate.

1,1′-Bis(diphenylphosphino)ferrocene[1] (dppf) and 1,1′-bis(diphenylphosphino)ruthenocene[2] (dppr) form stable complexes with a large variety of late transition metals and, as such, have manifold applications in organometallic chemistry and homogeneous catalysis. Since a relevant role in determining the chemistry and stereochemistry of the resultant metal complexes is played by the sandwiched metal, we decided to study the synthetic feasibility of the missing compound along the iron triad, i.e., 1,1′-bis(diphenylphosphino)osmocene (dppo), to complete the series and possibly establish a reactivity trend. In this communication, we present a brief account of our successful attempt to prepare dppo and outline the great potential of this potentially tridentate ligand in homogeneous catalysis.

dppo was prepared via lithiation of osmocene in *n*-hexane/diethyl ether, followed by reaction with chlorodiphenylphosphine. The yields were acceptable (25−30%), yet lower than those reported for both dppf[3] and dppr[2b] using comparable procedures, which reflects the lower propensity to metalation of osmocene as compared to ferrocene and ruthenocene.[3,4]

The plain reactions of dppo with $PdCl_2(PhCN)_2$ and PdCl(Me)(cod) gave $PdCl_2$(dppo) (**1**) and PdCl(Me)(dppo) (**2**), respectively (Scheme 1). Complexes **1** and **2** are key compounds to enter the organometallic chemistry of the Pd−dppo system by treatment with halide scavengers. Silver tosylate rapidly and quantitatively transformed **1** in CH_2Cl_2 into the tosylate adduct [Pd(OTs)(dppo)]OTs (**3**), while silver triflate gave $[Pd(NCMe)(dppo)](OTf)_2$ (**4**) upon reaction in CH_2Cl_2/MeCN. Both compounds contain a tridentate (κ^3Os,P,P) dppo ligand as a result of the replacement of the strong chloride donors by relatively weak ligands such as H_2O and MeCN. The osmium-centered e_{2g} electron density apparently competes for coordination with a second molecule of either water or acetonitrile. The removal of the chloride ligand with $NaBAr'_4$ from **2** in CH_2Cl_2 generated the κ^3-dppo complex $[Pd(Me)(dppo)]BAr'_4$ (**5**), which was converted into the acyl derivative $[Pd(COMe)(dppo)]BAr'_4$ (**6**) by reaction with CO.

Both dppo and its Pd(II) complexes were unambiguously identified by multinuclear NMR spectroscopy that, inter alia, provided a simple diagnostic tool for distinguishing the κ^2P,P and κ^3Os,P,P coordination modes of dppo. Indeed, as previously observed for Pd(II) complexes with dppf and dppf-related ligands,[5−7] the intramolecular formation of M→Pd bonds causes a remarkable high-field shift of the phosphorus resonance as compared to κ^2P,P derivatives. As an example, the

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[1] (a) Gan, K.-S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; Wiley-VCH: Weinheim, Germany, 1995; Chapter 1, p 13. (b) Colacot, T. J. *Platinum Met. Rev*. **2001**, *45*, 22. (c) Fong, S.-W. A.; Hor, T. S. A. *J. Cluster Sci*. **1998**, *9*, 351.

[2] (a) Yeo, S. P.; Henderson, W.; Mak, T. C.; Hor, T. S. A. *J. Organomet. Chem*. **1999**, *575*, 171. (b) Li, S.; Wei, B.; Low, P. M. N.; Lee, H. K.; Hor, T. S. A.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 1289. (c) Wei, B.; Li, S.; Lee, H. K.; Hor, T. S. A. *J. Organomet. Chem*. **1997**, *527*, 133 and references therein. (d) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 149.

[3] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem*. **1971**, *27*, 241.

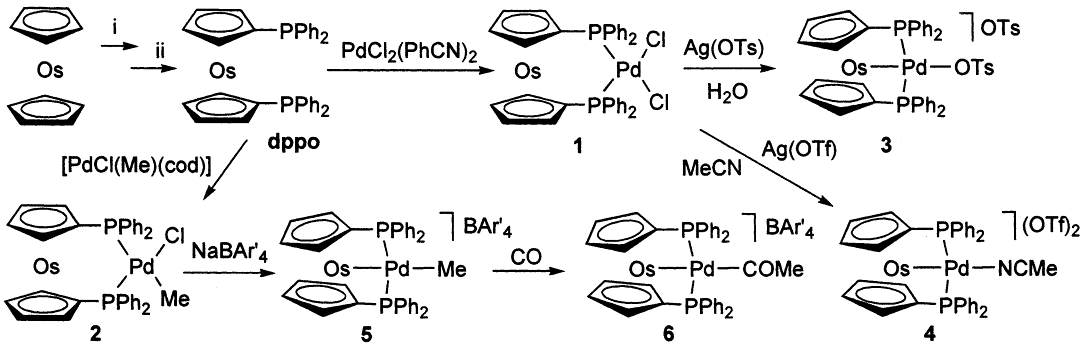
[4] (a) Abel, E. W.; Long, N. J.; Osborne, A. G.; Hursthouse, M. B.; Mazid, M. A. *J. Organomet. Chem*. **1992**, *430*, 117. (b) Akabori, S.; Munegumi, H.; Habata, Y.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Bull. Chem. Soc. Jpn*. **1985**, *58*, 2185.

[5] Sato, M.; Shigeta, H.; Sekino, M. *J. Organomet. Chem*. **1993**, *458*, 199.

[6] Gusev, O. V.; Kalsin, A. M.; Peterleitner, M. G.; Petrovskii, P. V.; Lyssenko, K. A.; Akhmedov, N. G.; Bianchini, C., Oberhauser, W.; Meli, A. *Organometallics* **2002**, *21*, 3637.

10.1021/om0208366 CCC: $25.00

Scheme 1. Synthesis of dppo and Palladium(II) Complexes[a]



[a] Legend: (i) ^{n}BuLi/TMEDA; (ii) PPh_2Cl. Abbreviations: Ar′ = 3,5-$(CF_3)_2C_6H_3$; OTf = trifluoromethanesulfonate; OTs = *p*-toluenesulfonate.

$^{31}P\{^1H\}$ NMR spectrum of **4** shows a singlet at −18.3 ppm for the two magnetically equivalent P nuclei that resonate at 37.9 ppm in the dichloride precursor **1**. The presence of Os−Pd bonds in **3**−**6** can also be inferred by the large chemical shift difference between the α- and β-hydrogen/carbon atoms of the cyclopentadienyl rings as compared to κ^2P,P complexes.[5−7] A single-crystal X-ray analysis removed any residual doubt, if any, regarding the presence of a Os−Pd bond in **4**·$2CH_2Cl_2$. An ORTEP drawing of the complex cation is provided in Figure 1.[8] The coordination geometry around palladium can be described as slightly distorted square planar with trans phosphorus atoms (P(1)−Pd(1)−P(2) = 164.9(1)°). Similar angles have been reported for $[Pd(PPh_3)(dppf)](BF_4)_2$[5] and [Pd(Me)(dtpf)]OTf[7b] (dtpf = 1,1′-bis(di-*tert*-butylphosphino)ferrocene). The coordination polyhedron of the palladium center is completed by osmium and an η^1-N MeCN ligand. The Os−Pd distance (2.840(1) Å) is consistent with a strong bonding interaction and is apparently responsible for the tilting of the Cp rings outward from the palladium atom by 28.2°. The Cp rings are eclipsed, which is unusual for palladium complexes with either dppf or dppr.[1−3]

The formation of stable Pd−methyl and Pd−acyl compounds anticipated the potential of dppo−Pd(II) complexes as catalyst precursors for the carbonylation of olefins.[6,9] Indeed, a study of the methoxycarbonylation of ethene has revealed that the tosylate complex **3** is an effective catalyst for the selective production of methyl propanoate (Scheme 2a).[10] The remarkable selectivity exhibited by **3** contrasts dramatically with that of the dppf precursor $[Pd(H_2O)_2(dppf)](OTs)_2$, which, under comparable reaction conditions, produces various low-molecular-weight oxygenates spanning from methyl propanoate to alternating polyketones.[6] Preliminary studies of ethene methoxycarbonylation by palladium(II) catalysts modified with dppf, dppr, or dppo have shown that the formation of dative M−Pd bonds (hence of complexes with a trans arrangement of the phosphorus atoms) favors the selective production of methyl

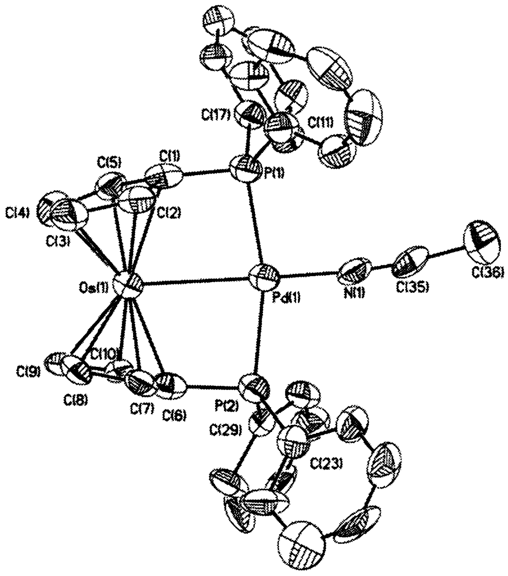
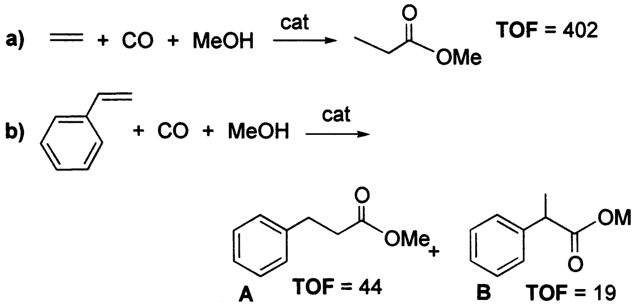


Figure 1. ORTEP drawing of **4**·$2CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level. The OTf anion is omitted for clarity. Select bond lengths (a) and angles (deg): Pd−P1 = 2.259(3); Pd−P2 = 2.272(3); Pd−Os = 2.840(1); Pd−N = 1.885(11); P1−Pd−P2 = 164.87(14); Os−Pd−N = 179.1(3).

Scheme 2. Methoxycarbonylation of Ethene (a) and Styrene (b) with 3 as Precatalyst[a]



[a] Conditions: (a) catalyst 0.01 mmol, 1:1 CO/C_2H_4, 600 psi (constant pressure), TsOH 0.4 mmol, solvent 100 mL, 85 °C, 1 h; (b) catalyst 0.01 mmol, styrene 2 mmol, CO, 800 psi, TsOH 0.4 mmol, solvent 20 mL, 80 °C, 3 h. TOF is given in units of mol of product ((mol of cat) h)$^{-1}$.

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(7) (a) Zuideveld, M. A.; Swennenhuis, B. H. G.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **2001**, 637, 805. (b) Zuideveld, M. A.; Swennenhuis, B. H. G.; Boele, M. D. K.; Guari, Y.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **2002**, 2308.

(8) Crystal data: $C_{40}H_{35}Cl_4F_6NO_6S_2OsP_2Pd$, T = 110(2) K, orthorhombic, space group $Pca2_1$, a = 26.438(5) Å, b = 16.967(3) Å, c = 10.272(2) Å, V = 4608(1) Å^3, Z = 4, D_{calcd} = 1.880 g cm^{-3}, μ = 3.608 mm^{-1}, F(000) = 2544, 13 121 reflections, GOF = 0.854, R indices ($I > 2\sigma(I)$) R1 = 0.0490 and wR2 = 0.0713.

(9) Beller, M.; Tafesh, A. M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Hermann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 1996; p 187.

(10) Robertson, R. A. M.; Cole-Hamilton, D. J. *Coord. Chem. Rev.* **2002**, *225*, 67.

propanoate, while the propensity to form M−P bonds increases in the order Fe < Ru < Os.[11]

Good selectivity was also exhibited in the carbonylation of styrene, which gave exclusively the saturated esters methyl 3-phenylpropanoate (**A**) and methyl 2-phenylpropanoate (**B**) (Scheme 2b).[9,12−14] No comparison with either dppf or dppr palladium complexes can be made for the absence of appropriate reports in the literature. Under the present experimental conditions, both Pd−OMe and Pd−H catalysis initiators may form.[15] The former species will generate **A** via CO insertion, followed by 2,1-insertion of styrene into Pd−COOMe and protonolysis.[13] Starting from Pd−H, both **A** and **B** may form, depending on the insertion mechanism of styrene (both 1,2- and 2,1-modes are possible, in fact), followed by CO insertion into a Pd−styryl bond and termination by methanolysis.[14b,16]

Acknowledgment. Thanks are due to the EC for support under Contract No. HPRN-CT-2002-00196, to a CNR-RAS bilateral agreement, to the Russian Foundation for Basic Research (Grant Nos. 00-03-32855 and 01-03-06145), and to the Haldor Topsøe A/S.

Supporting Information Available: Text giving synthetic procedures for ligand and palladium complexes with full spectroscopic and elemental characterization data and tables of bond lengths and angles and positional and thermal parameters for the complex $\mathbf{4}\cdot 2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0208366

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(11) Bianchini, C.; Meli, A.; Oberhauser, W. Manuscript in preparation.

(12) Bianchini, C.; Mantovani, G.; Meli, A.; Oberhauser, W.; Brüggeller, P.; Stampfl, T. *J. Chem. Soc., Dalton Trans.* **2001**, 690.

(13) (a) Aeby, A.; Gsponer, A.; Consiglio, G. *J. Am. Chem. Soc.* **1998**, *120*, 11000. (b) Sperrle, M.; Consiglio, G. *Chem. Ber.* **1997**, *130*, 1557. (c) Pisano, C.; Mezzetti, A.; Consiglio, G. *Organometallics* **1992**, *11*, 20.

(14) (a) Seyad, A.; Kelkar, A. A.; Toniolo, L.; Chaudari, R. V. *J. Mol. Catal. A* **2000**, *151*, 47. (b) Seyad, A.; Jayasree, S.; Damodoran, K.; Toniolo, L.; Chaudari, R. V. *J. Organomet. Chem.* **2000**, *601*, 100. (c) Del Rio, I.; Ruiz, N.; Claver, C.; van der Veen, L. A.; van Leeuwen, P. W. N. M. *J. Mol. Catal. A* **2000**, *161*, 39.

(15) Milstein, D. *Acc. Chem. Res.* **1988**, *212*, 428.

(16) Tooze, R. P.; Whiston, K.; Molyan, V.; Taylor, M. J.; Wilson, N. W. *J. Chem. Soc., Dalton Trans.* **2000**, 3441.