5412 *Organometallics* **1999,** *18,* 5412−5415

X-ray Diffraction Studies of Group 9 Transition-Metal Complexes Containing an sp^3 C−H Activated Functionalized Triphenylphosphine

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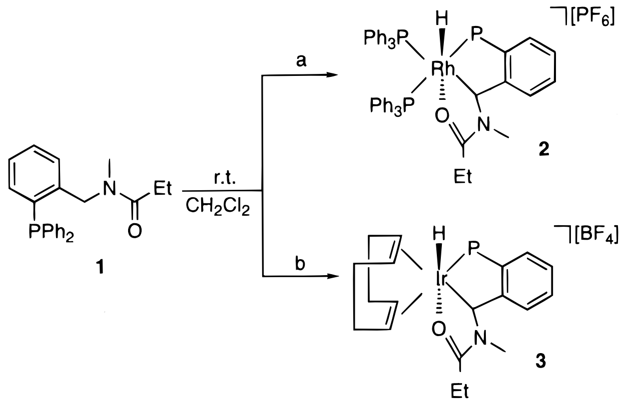
Received July 20, 1999

Summary: Treatment of the hemilabile tertiary phosphino amide o-$Ph_2PC_6H_4CH_2N(Me)C(O)Et$ (DPPBA; ***1****) with the appropiate Rh(I) or Ir(I) precursor complex results in cyclometalation by oxidative addition of the benzylic C−H bond to the metal center. The solution structures of the two synthesized complexes [$RhH(PPh_3)_2$(DPPBA)][PF_6] (****2****) and [IrH(1,5-COD)(DPPBA)][BF_4] (****3****) have been unambiguously identified by various NMR spectroscopic techniques. Also, single-crystal X-ray diffraction studies have been performed for* ***2*** *and* ***3****. These are the first crystal structures obtained with DPPBA as a ligand, giving final confirmation of the capability of* ***1*** *to trischelate in platinum group metal complexes.*

Introduction

Transition-metal complexes with tridentate PCP-type ligands were first reported in the early 1970s[1] and have been extensively studied since.[2] These structurally well-defined complexes, and the related compounds with NCN or SCS ligands,[3] have proved to be excellent catalytic precursors over a wide range encompassing dehydrogenation,[4] coupling,[5] addition,[6] insertion,[7] and asymmetric[8] reactions. However, metal insertion into an sp^3 C−H bond, instead of a C−H aryl bond, would result in a more electron-rich metal center, which may alter the catalytic activity. A recent comparative study by Ohff et al. showed that a Pd(II) PCP-type complex, formed by palladium insertion into an sp^3 C−H bond of 1,3-bis[(diisopropylphosphino)methyl]-2,4,6-trimethylbenzene, was indeed a remarkable active catalyst in the Heck reaction.[9] To develop new functionalized tertiary phosphines capable of forming tridentate metallacycles by intramolecular metal insertion into sp^3 C−H bonds could be of importance in catalysis.

Scheme 1



(a) = H_2, [Rh(2,5-NBD)$(PPh_3)_2$][PF_6]
(b) = [Ir(1,5-COD)$_2$][BF_4]
Phenyls on DPPBA are omitted for clarity in **2** and **3**.

We have recently published an article elucidating the coordination chemistry of the ligand DPPBA (**1**) (*N*-methyl-*N*-propionyl-2-(diphenylphosphino)benzylamine) in different rhodium complexes.[10] There were strong indications that this potential PCO-type ligand coordinates tridentately by oxidative addition of a benzylic C−H bond to the rhodium center, given the right conditions. In this paper we would like to give final confirmation of this by presenting the first crystal structures obtained with **1** as a ligand coordinating in a PCO manner in platinum group metal complexes.

Result and Discussion

Synthesis and Spectroscopic Properties. To achieve oxidative insertion of a rhodium center into ligand **1**, it is necessary to generate a species having a metal center with high electron density and vacant coordination sites.[10] Accordingly, complex **2** could only be synthesized by treating the precursor [Rh(2,5-NBD)-$(PPh_3)_2$][PF_6] with ligand **1** under an atmosphere of dihydrogen (Scheme 1) and thereby removing the π-accepting diene from the coordination sphere. The resulting complex was unambiguously characterized by vari-

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10.1021/om990563n CCC: $18.00

ous NMR spectroscopic techniques. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits an ABCX pattern; two doublet of doublet of doublet resonances at 54.8 ($^1J_{RhP} = 114$ Hz, $^2J_{PP} = 383$, 23 Hz) and 40.1 ppm ($^1J_{RhP} = 110$ Hz, $^2J_{PP} = 383$, 23 Hz) and a doublet of triplets at 26.2 ppm ($^1J_{RhP} = 87$ Hz, $^2J_{PP} = 23$ Hz). In the ^1H NMR spectrum the Rh−H group gives rise to a doublet of quartets positioned at −16.5 ppm ($^1J_{RhH} = 7.3$ Hz, $^2J_{PH} = 16.9$ Hz), which collapses to a doublet in $^1H\{^{31}P\}$ NMR. In addition, the remaining benzylic proton resonates at 4.30 ppm ($^3J_{PH} = 19.8$ Hz). The benzylic carbon appears in the $^{13}C\{^1H\}$ NMR as an unresolved multiplet at 73.1 ppm. Also, the IR spectrum reveals both a Rh−H band (2117 cm^{-1}) and a coordinating C═O stretching frequency (1570 cm^{-1}). X-ray crystallography of **2** has been carried out, and all spectroscopic evidence suggests that the solution and solid-state structures are the same.

As we will see, when using the last member of group 9 as the transition-metal center, it is not essential to generate a complex exclusively with σ-donors to achieve metallacyclic formation with **1** as a ligand (cf. complex **2**). Complex **3** was obtained by treating a dichloromethane solution of the diene complex $[Ir(1,5\text{-}COD)_2][BF_4]$ with **1**. The obtained set of NMR data strongly suggest the configuration of **3** in solution to be as depicted in Scheme 1. In the $^{31}P\{^1H\}$ NMR spectrum a singlet at 33.2 ppm is observed. Metal insertion at the benzylic group results in two doublets at 5.32 ($^3J_{PH} = 2.7$ Hz) and −17.8 ppm ($^2J_{PH} = 11.7$ Hz) exhibited in the ^1H NMR spectrum and a doublet at 61.6 ppm ($^2J_{PC} = 6.7$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum. HMQC NMR spectroscopy verifies these assignments. Furthermore, the positions of the Ir−H (2195 cm^{-1}) and the C═O (1581 cm^{-1}) stretches in the IR spectrum also indicate the hydride to be apical and coordination of the carbonyl functionality. Final confirmation of a metallacyclic structure in **3** has been obtained by X-ray crystallography.

X-ray Diffraction Studies. The convincing spectroscopic evidence suggesting complex **2** to be the result of an oxidative addition of a benzylic C−H bond to the rhodium center has been supported by a single-crystal X-ray analysis. Colorless blocks of **2** were obtained upon crystallization by layering diethyl ether onto a chloroform solution. Four chloroform molecules are present in the triclinic unit cell. A perspective view of the molecular structure is shown in Figure 1, including selected bond distances and angles.

The complex has a distorted-octahedral configuration in which the rhodium center is surrounded in the equatorial plane by the three phosphorus atoms and the metalated carbon atom. The apical positions are occupied by the strongest trans director, the hydride ligand, being located trans to the weakest one, the carbonyl oxygen atom. The Rh−P1 and Rh−P3 bond distances are of normal magnitude,[11] and the significantly longer Rh−P2 bond distance (2.411(1) Å) manifests the strong trans influence exerted by the C5 atom. Note the correlation between the rhodium−phosphorus bond lengths and the positions of the individual phosphorus resonances in the $^{31}P\{^1H\}$ NMR spectrum. The bond length between the sp^3-hybridized carbon and the rhodium atom (Rh−C5 = 2.123(6) Å), as well as the Rh−H1 (1.46(6) Å) bond distance, is in agreement with the values observed in other metalated Rh(III) species.[12] The cyclometalated trischelating DPPBA ligand is displaying a *fac* arrangement around the rhodium atom, resulting in two five-membered chelate rings. Both the P1−Rh−C5 (80.04(17)°) and C5−Rh−O (79.89(19)°) angles are acute due to ring strain, and the Rh−P1 and Rh−O bonds are nearly perpendicular to each other (P1−Rh−O angle is 90.88(12)°).

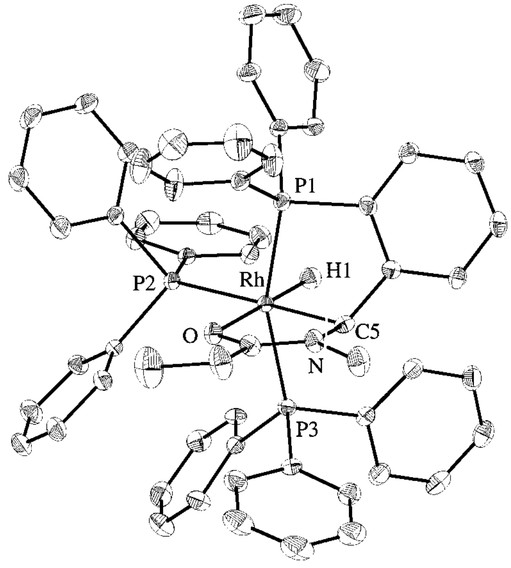

Figure 1. Perspective view (ORTEP) of cation **2**. Bond distances (Å) and angles (deg) with estimated standard deviations: Rh−P1 = 2.317(2); Rh−P2 = 2.411(1); Rh−P3 = 2.354(2); Rh−O = 2.150(4); Rh−C5 = 2.123(6); Rh−H1 = 1.46(6); P1−Rh−P2 = 99.63(6); P1−Rh−P3 = 160.46(5); P1−Rh−C5 = 80.04(17); P1−Rh−O = 90.88(12); C5−Rh−O = 79.89(19).

For the definite characterization of complex **3**, a single-crystal X-ray diffraction analysis was carried out. Slow vapor diffusion of diethyl ether into a dichloromethane solution led to the deposition of **3** as colorless blocks. The triclinic unit cell belongs to the space group $P\bar{1}$. A view of the molecular structure is shown in Figure 2, including selected bond distances and angles.

The coordination geometry about the iridium center can be rationalized as a distorted octahedron, where the equatorial plane is constituted by the phosphorus and nitrogen atoms and the midpoints of the η^2:η^2 coordinating diene. As for complex **2**, the apical positions are occupied by the hydride and the carbonyl oxygen atom. The observed Ir−H1 bond distance (1.57(8) Å) is in good agreement with those established for other hydridoiridium(III) complexes.[13] The hydride, one alkene π-bond, and the iridium center are coplanar, but clearly the exclusive cis addition of the metal hydride to the diene does not take place,[14] a phenomenon seen in other

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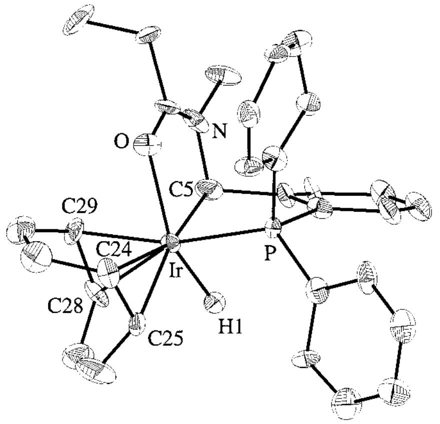

Figure 2. Perspective view (ORTEP) of cation **3**. Bond distances (Å) and angles (deg) with estimated standard deviations: Ir−P = 2.284(2); Ir−O = 2.149(4); Ir−C5 = 2.082(6); Ir−C24 = 2.276(7); Ir−C25 = 2.285(7); Ir−C28 = 2.270(6); Ir−C29 = 2.244(7); Ir−H1 = 1.57(8); C24−C25 = 1.364(12); C28−C29 = 1.375(10); P−Ir−C5 = 82.2(2); P−Ir−O = 89.1(1); C5−Ir−O = 80.3(2).

related complexes.[15] The Ir−P bond distance (2.284(2) Å) matches well the values reported for other iridium−phosphine complexes[11] and is very close to that established for the related cyclometalated phosphino ester complex $[IrH(1,5\text{-}COD)(2\text{-}Ph_2PC_6H_4CHOC(O)Et)][BF_4]$.[13c] Also, the Ir−O bond length (2.149(4) Å) is somewhat shorter than in the aforementioned complex, probably reflecting a slightly stronger donor strength for the amide than for the ester group. In fact, the interaction between the iridium and oxygen atoms is strong since it is close to the sum of the covalent radii (2.02 Å). The Ir−C5 bond distance (2.082(6) Å) falls within the range reported for other sp^3-cyclometalated hydridoiridium(III) complexes.[16] In contrast to complex **2** there is just a slight difference in trans influence between the C5 and the P donor atoms, reflected by the following properties: (i) the Ir−C(olefin) bond distances for Ir−C24 and Ir−C25 are 2.276(7) and 2.285(7) Å, respectively, compared to the values for Ir−C28 (2.270(6) Å) and Ir−C29 (2.244(7) Å); (ii) the respective bond distances between the sp^2-carbon atoms in the diene ligand are 1.364(12) Å for C24−C25 and 1.375(10) Å for C28−C29. As for complex **2**, the cyclometalated DPPBA ligand is capping one triangular face of the octahedron in which the P−Ir−C5 and C5−Ir−O angles are acute (82.2(2)° and 80.3(2)°, respectively) and the Ir−P and Ir−O bonds are nearly perpendicular to each other (P−Ir−O angle is 89.1(1)°).

In summary, these crystallographic investigations have clearly shown that the triphenyl phosphine derivative DPPBA (**1**) does oxidatively add one of its benzylic C−H bonds to platinum group metals, given the right conditions. In doing so it adopts a *fac* configuration, and the resulting hydride ultimately resides in an apical position trans to the coordinated carbonyl functionality.

Experimental Section

The general procedures and purification of solvents have been previously described.[10] Commercially available reagents were purchased and used without further purification. The phosphine DPPBA (**1**)[17] and the complexes $[Ir(1,5\text{-}COD)_2][BF_4]$[18] and $[Rh(2,5\text{-}NBD)(PPh_3)_2][PF_6]$[19] were prepared according to literature procedures.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 300, 121, and 75 MHz, respectively, using a Varian Unity 300 MHz spectrometer. HMQC (2D inverse ^1H, ^{13}C correlation) NMR spectra were recorded at 500 MHz using a Bruker ARX 500 MHz spectrometer. All NMR measurements were performed in $CDCl_3$. Infrared spectra were recorded on a Bio-Rad FTS 6000 FT-IR spectrometer. Melting points were determined in argon-sealed capillary tubes and are uncorrected. Elemental analyses were performed by AB Mikro Kemi, Uppsala, Sweden.

Reaction of $[Rh(2,5\text{-}NBD)(PPh_3)_2][PF_6]$ with 1. Formation of $[RhH(PPh_3)_2(DPPBA)][PF_6]$ (2). A red dichloromethane solution (10 mL) of DPPBA (**1**; 140 mg, 0.162 mmol) and $[Rh(2,5\text{-}NBD)(PPh_3)_2][PF_6]$ (58.8 mg, 0.163 mmol) was cooled to −10 °C. The argon atmosphere was replaced by molecular hydrogen, and the solution was allowed to reach room temperature. After 1 h the solution was yellow and once again the atmosphere was replaced, this time from dihydrogen to argon. Upon leaving the solution for half an hour, it turned slightly brown. The solvent was concentrated under vacuum to ca. 2 mL, and addition of diethyl ether yielded an off-white precipitate. The suspension was filtered in air and washed with diethyl ether (2 × 10 mL) and *n*-hexane (2 × 10 mL). Isolated yield: 169 mg (92%). $^{31}P\{^1H\}$ NMR: δ 54.8 (ddd, $^1J_{RhP} = 114$ Hz, $^2J_{PP} = 383$, 23 Hz), 40.1 (ddd, $^1J_{RhP} = 110$ Hz, $^2J_{PP} = 383$, 23 Hz), 26.2 (dt, $^1J_{RhP} = 87$ Hz, $^2J_{PP} = 23$ Hz), −143.7 (sept, $^1J_{PF} = 712$ Hz). ^1H NMR: δ 7.42−7.02 (m, 42H, Ar), 6.75 (bt, $^3J_{HH} = 8.2$ Hz, 1H, Ar), 5.96 (bt, $^3J_{HH} = 9.4$ Hz, 1H, Ar), 4.30 (d, $^3J_{PH} = 19.8$ Hz, 1H, Ar−C(R)*H*−Rh), 1.91 (s, 3H, N−CH_3), 1.27−0.82 (m, 2H, −CH_2−), 0.73 (bt, $^3J_{HH} = 6.4$ Hz, 3H, −CH_3), −16.5 (dq, $^1J_{RhH} = 7.3$ Hz, $^2J_{PH} = 16.9$ Hz, 1H, Rh−*H*)). $^{13}C\{^1H\}$ NMR: δ 179 (s, −*C*(O)−), 152−128 (md, Ar), 73.1 (m, Ar−*C*(R)H−Rh), 34.1 (s, N−*C*H_3), 26.7 (s, −*C*H_2−), 7.92 (s, −*C*H_3), (assignment of ^1H and $^{13}C\{^1H\}$ NMR signals were confirmed by $^1H\{^{31}P\}$ and HMQC NMR experiments). IR (KBr): 2117 cm^{-1} (w, Rh−H), 1570 cm^{-1} (s, C=O); mp 165−170 °C dec. Anal. Calcd for $C_{59}H_{54}F_6NOP_4Rh$: C, 62.5; H, 4.8; P, 10.9. Found: C, 62.3; H, 5.1; P, 10.6.

Reaction of $[Ir(1,5\text{-}COD)_2][BF_4]$ with 1. Formation of $[IrH(1,5\text{-}COD)(DPPBA)][BF_4]$ (3). When $[Ir(1,5\text{-}COD)_2][BF_4]$ (102 mg, 0.206 mmol) and DPPBA (**1**; 74.4 mg, 0.206 mmol) were mixed in dichloromethane (10 mL), the solution gradually changed color from dark red to light yellow within minutes. After 30 min an off-white powder was isolated by evaporation of the solvent, which was sequentially washed in air with diethyl ether (3 × 10 mL) and *n*-hexane (3 × 10 mL). Isolated yield: 125 mg (81%). $^{31}P\{^1H\}$ NMR: δ 33.2 (s). ^1H NMR: δ 7.75−6.94 (m, 14H, Ar), 5.70 (m, 1H, COD), 5.32 (d, $^3J_{PH} = 2.7$ Hz, 1H, Ar−C(R)*H*−Ir), 5.01 (m, 1H, COD), 4.55 (m, 1H, COD), 4.43 (m, 1H, COD), 2.89 (s, 3H, N−CH_3), 2.56−2.30 (m, 8H, COD), 2.16 (m, 1H, −CH_2−), 1.48 (m, 1H, −CH_2−), 0.60 (t, $^3J_{HH} = 7.3$ Hz, 3H, −CH_3), −17.8 (d, $^2J_{PH} = 11.7$ Hz, 1H, Ir−*H*); $^{13}C\{^1H\}$ NMR: δ 180 (s, −*C*(CO)−), 156−125 (md, Ar), 97.1 (d, $^2J_{PC} = 14.8$ Hz, COD), 96.6 (m, COD), 90.4 (s, COD), 88.8 (s, COD), 61.6 (d, $^2J_{PC} = 6.7$ Hz, Ar−*C*(R)H−Ir), 35.5 (s, COD), 33.1 (s, N−*C*H_3), 32.9 (s, COD), 29.2 (s, COD), 27.8 (s, COD), 26.7 (s, −*C*H_2−), 8.1 (s, −*C*H_3) (assignment of ^1H and $^{13}C\{^1H\}$ NMR signals were confirmed by $^1H\{^{31}P\}$ and HMQC

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Table 1. Crystallographic Data for Complexes 2 and 3

formula	$C_{59}H_{54}F_6NOP_4Rh$ (**2**) + $2CHCl_3$	$C_{31}H_{36}BF_4IrNOP$ (**3**)
fw	1372.56	748.59
cryst size, mm^3	0.26 × 0.18 × 0.11	0.21 × 0.16 × 0.09
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.4288(9)	10.3296(5)
b, Å	15.4089(11)	11.4514(6)
c, Å	16.3996(12)	13.3332(8)
α, deg	88.746(2)	79.426(1)
β, deg	87.840(2)	77.561(1)
γ, deg	79.276(2)	77.746(1)
V, $Å^3$	3083.4(4)	1489.3(1)
Z	2	2
d_{calcd}, g cm^{-3}	1.478	1.669
diffractometer	smart CCD system	smart CCD system
radiation (graphite monochr)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
temp, K	293(2)	293(2)
μ, mm^{-1}	0.700	4.587
scan method	ω	ω
2θ(max), deg	50	55
abs corr[20]	ω-scan/multiscan	ω-scan/multiscan
T_{min}	0.831	0.372
T_{max}	0.926	0.662
R_{int}[23]	0.0576	0.0493
total no. of rflns	18646	10846
no. of unique rflns	10809	6787
no. of obsd rflns ($2\sigma(I)$)	5871	5552
no. of params refined	724	379
R[24]	0.0606	0.0580
R_w[25]	0.1262	0.1110
rfln:param ratio	14.93	17.91
resid electron density, e $Å^{-3}$	0.848	1.670

NMR experiments). IR (KBr): 2195 cm^{-1} (m, Ir−H), 1581 cm^{-1} (s, C═O); mp 188−193 °C dec. Anal. Calcd for $C_{31}H_{36}BF_4IrNOP$: C, 49.7; H, 4.8; P, 4.1. Found: C, 49.5; H, 4.9; P, 4.0.

X-ray Structural Analyses of Complexes 2 and 3. Single crystals were grown from chloroform/diethyl ether (**2**) and dichloromethane/diethyl ether (**3**) solutions at room temperature. The crystal data, data collection, and refinement details are provided in Table 1. Intensity data were collected at 293 K with a Smart CCD system using ω scans and a rotating anode with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). All reflections were corrected for Lorentz and polarization effects as well as absorption.[20] No significant changes in intensities were noticed throughout the data collections.

The structures were solved by Patterson methods using SHELXS-97,[21] while the structure refinements were performed on F^2 using SHELXL-97.[22] All non-H atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were constrained to parent sites, using a riding model. The coordinated hydrides in **2** and **3**, respectively, were located from the difference Fourier map after anisotropic refinement, and then the hydrides were isotropically refined. No high electron density residues were found in the structures.

Acknowledgment. Financial support by the TFR (The Swedish Research Council for Technological Sciences) and the NFR (The Swedish Natural Science Research Council) is gratefully acknowledged.

Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **2** and **3**. Figures of complexes **2** and **3** showing complete atomic numbering. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990563N

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(23) $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum|F_o^2|$.

(24) $R = \sum|F_o| - |F_c||/\sum|F_o|$.

(25) $R_w = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]$.