Table III. Selected Angles (Deg)

O(1)–U–O(2)	179.1 (4)	O(7)–U–O(8)	49.9 (3)
O(1)–U–O(3)	91.0 (3)	U–O(3)–U	112.3 (3)
O(1)–U–O(3)[a]	88.6 (3)	O(5)–O(3)–N(3)	103.6 (4)
O(1)–U–O(4)	85.9 (3)	O(5)–N(1)–O(4)	121 (1)
O(1)–U–O(6)	95.0 (3)	O(5)–N(1)–O(6)	123 (1)
O(1)–U–O(7)	90.5 (4)	O(4)–N(1)–O(6)	116 (1)
O(1)–U–O(8)	87.5 (3)	O(7)–N(2)–O(8)	115 (1)
O(2)–U–O(3)	89.3 (4)	O(7)–N(2)–O(9)	123 (1)
O(2)–U–O(3)[a]	90.8 (3)	O(8)–N(2)–O(9)	123 (1)
O(2)–U–O(4)	93.8 (4)	C(1)–N(3)–C(2)	108 (1)
O(2)–U–O(6)	84.2 (4)	N(3)–C(2)–C(3)	108 (1)
O(2)–U–O(7)	90.1 (4)	C(2)–C(3)–N(4)	107 (1)
O(2)–U–O(8)	93.3 (4)	C(3)–N(4)–C(1)	109 (1)
O(3)–U–O(3)	67.7 (3)	N(3)–C(1)–N(4)	109 (1)
O(4)–U–O(6)	49.3 (3)		

[a] At position $-x, -y, -z$.

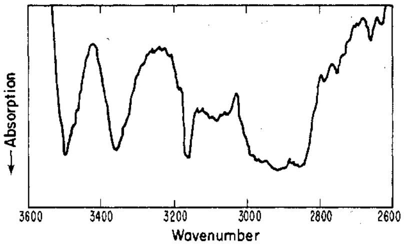

Figure 2. Infrared spectrum of the title compound taken as a Nujol mull.

Uranium is eight-coordinate at the center of a distorted hexagonal bipyramid which has the uranyl oxygen atoms at the apices. The O–U–O axis is more or less perpendicular to the distorted equatorial plane; the largest deviation from orthogonality of the O–U–O axis to any U–O bond in the equatorial plane is 6°. A slight twist of the nitrate groups out of the equatorial plane indicates some crowding in the coordination environment about UO_2^{2+}. The geometry and bond distances of the water-bridged uranyl dimer in this structure are remarkably similar to the hydroxy-bridged uranyl dimer found in $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3]\cdot H_2O$,[20] in which hydroxide instead of H_2O is the bridging group and three waters occupy one end of the dimer rather than two nitrate groups. Another similar type of uranyl dimer is found in the $Cl(H_2O)_3UO_2(OH)_2UO_2(H_2O)_3Cl$ structure,[21] which has heptacoordinate rather than octacoordinate uranium. The U–U distance in the title compound is 3.927 Å and compares to 3.939 Å[20] and 3.944 Å[21] in the two other compounds mentioned above. The bridging U–O(water) distances are about 0.2 Å shorter than the U–O(nitrate) distances, and this is consistent with what is observed in the other compounds.[20,21] The double oxygen bridging of the uranyl ion is somewhat rare, but several examples exist for thorium in which the Th–Th distances vary from 3.97 to 4.09 Å in a series of double hydroxo-bridged thorium(IV) complexes.[22]

The imidazole molecules are associated by hydrogen bonds to the bridging water molecules and are not directly bonded to the uranyl cations. The bond distances and angles of the imidazole molecules are in agreement with previous structural studies.[23,24]

The infrared spectrum of the complex is quite distinctive in the O–H and N–H stretching region and is shown in Figure 2. Rather than the broad band in the 3500-cm^{-1} region which is customarily seen for metal-ion complexes involving water, a single, considerably sharpened peak is found at 3500 cm^{-1}. An N–H stretching band, similar in contour to the O–H band, is found at 3350 cm^{-1}, while a second, sharper N–H frequency lies at 3160 cm^{-1}. These values compare quite favorably with those of transition-metal–imidazole complexes.[25]

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Registry No. $[UO_2(NO_3)_2(H_2O)]_2\cdot 2C_3H_4N_2$, 72827-60-2.

Supplementary Material Available: Data processing formulas, the table of anisotropic thermal parameters, the calculated powder pattern, and the listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(20) Perrin, A. *Acta Crystallogr., Sect. B* **1976**, *32*, 1658.
(21) Aberg, M. *Acta Chem. Scand.* **1969**, *23*, 791.
(22) Johansson, G. *Acta Chem. Scand.* **1968**, *22*, 389 and references therein.
(23) Hsu, I. N.; Craven, B. M. *Acta Crystallogr., Sect. B* **1974**, *30*, 988.
(24) Craven, B. M.; McMullan, R. K.; Bell, J. D.; Freeman, H. C. *Acta Crystallogr., Sect. B* **1977**, *33*, 2585.
(25) Davis, W. J.; Smith, J. *J. Chem. Soc. A* **1971**, 317.

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Interaction of Carbon Dioxide with Coordinatively Unsaturated Rhodium(I) Complexes with the Ligand 1,2-Bis(diphenylphosphino)ethane

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The activation of CO_2 through coordination to transition-metal complexes[2] has received considerable attention in the last few years as these complexes can be involved in CO_2 fixation into organic substrates.

A number of CO_2 complexes of Rh(I) with monodentate phosphines have been isolated,[3] and reports on the interaction of CO_2 with Rh(I) complexes with chelating ligands such as 1,2-bis(dimethylphosphino)ethane or 1,2-bis(diethylphosphino)ethane[4] can be found in the literature, but no evidence of CO_2 coordination to Rh(I) or to other transition-metal complexes with the ligand 1,2-bis(diphenylphosphino)ethane (diphos) has been reported to date.

In this note we report the results of our studies on the interaction of CO_2 with unsaturated Rh(I) complexes with diphos and the synthesis, structure, and reactivity of the covalent complex Rh(diphos)(η-BPh_4).

Experimental Section

Reactions were carried out in an atmosphere of purified gases. The solvents were dried as reported in the literature and stored under nitrogen. Infrared spectra were run with a Perkin-Elmer 577 spectrophotometer. Molecular weights were determined with the Hewlett-Packard 302 VP osmometer, and gas chromatographic analyses were performed with a Hewlett-Packard 5750 instrument.

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(1) (a) University of Bari. (b) University of Milan.
(2) (a) C. Floriani and G. Facchinetti, *J. Chem. Soc., Chem. Commun.*, 615 (1974); (b) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *ibid.*, 636 (1975); (c) M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 708 (1977).
(3) (a) M. E. Vol'pin, I. S. Kolomnikov, and T. S. Lobeova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2084 (1969); (b) I. S. Kolomnikov, T. S. Belopotapova, T. S. Lysyak, and M. E. Vol'pin, *J. Organomet. Chem.*, **67**, C25 (1974); (c) Y. Iwashita and A. Hayada, *J. Am. Chem. Soc.*, **91**, 2525 (1969); (d) M. Aresta and C. F. Nobile, *Inorg. Chim. Acta*, **24**, L49 (1977).
(4) (a) A. D. English and T. Herskovitz, *J. Am. Chem. Soc.*, **99**, 1648 (1977); (b) T. Hershkovitz, *ibid.*, **99**, 2391 (1977).

Preparation of the Complexes. Preparation of $Rh(C_2H_4)(diphos)Cl$ and $[Rh(diphos)Cl]_2$. To a filtered solution of $[Rh(C_2H_4)_2Cl]_2$ (0.300 g, 0.77 mmol) in toluene (30 cm^3) was added diphos (0.615 g, 1.54 mmol) in toluene (20 cm^3), and the yellow precipitate formed was filtered, washed with pentane, and dried in vacuo at room temperature. Anal. Calcd for $C_{28}H_{28}ClP_2Rh$: C, 59.54; H, 5.0; Cl, 6.28; P, 10.97. Found: C, 59.6; H, 5.10; Cl, 6.30; P, 11.0.

When the yellow solid is heated above 100 °C, ethylene is evolved slowly (1 mol/Rh atom) and the complex converts to the orange dimer $[Rh(diphos)Cl]_2$. This reaction goes to completion in a short time at 160 °C. The dimer complex is obtained as well by prolonged stirring of a suspension of the ethylene complex in toluene at room temperature under nitrogen. Anal. Calcd for $C_{52}H_{48}Cl_2P_4Rh_2$: C, 58.18; H, 4.51; Cl, 6.60; P, 11.54. Found: C, 58.0; H, 4.50; Cl, 6.63; P, 10.98. The dimer is diamagnetic with mp 303 °C and ν(Rh–Cl) at 270 cm^{-1}, consistent with a chlorine-bridged structure.

Preparation of $Rh(diphos)(BPh_4)$. To a filtered solution of $[Rh(C_2H_4)_2Cl]_2$ (0.29 g, 0.74 mmol) in benzene (100 cm^3) was added diphos (0.59 g, 1.49 mmol) in benzene (15 cm^3), the resulting orange solution was pumped in vacuo in order to eliminate the evolved ethylene. To the clear solution was added $NaBPh_4$ (0.56 g, 1.64 mmol) in ethanol (5 cm^3), and the solution was stirred at room temperature. The orange microcrystalline solid formed was filtered, washed with water, cold ethanol, and pentane, and dried in vacuo: diamagnetic, stable in air; dec pt 230 °C. Anal. Calcd for $C_{50}H_{44}BP_2Rh$: C, 73.13; H, 5.3; P, 7.55. Found: C, 73.3; H, 5.25; P, 7.53. Crystallization from CH_2Cl_2 affords large crystals which contain traces of Cl due to some solvent of crystallization.

Preparation of $Rh(C_6H_5)(diphos)$. The complex $Rh(diphos)(BPh_4)$ (0.50 g, 0.61 mmol) was suspended in dry acetone (20 cm^3) in a Carius tube, sealed under N_2 or CO_2 (1 atm) and heated with shaking at 70 °C. The orange complex converted to a red crystalline complex. When the starting material had disappeared, the tube was cooled to room temperature and opened, and the red crystals were filtered, washed with acetone, and dried in vacuo. Crystallization from benzene afforded the pure compound, dec pt 207 °C. Anal. Calcd for $C_{32}H_{29}P_2Rh$: C, 66.3; H, 5.18; P, 10.70. Found: C, 66.0; H, 5.0; P, 10.65. The complex is diamagnetic and monomeric in CH_2Cl_2 (mol wt: calcd, 578; found, 555). Attempts to perform this reaction in halogenated solvents afforded partially halogenated Rh species.

Preparation of $Rh(OOC–C_6H_5)(diphos)$. CO_2 was condensed into a Carius tube containing a suspension of $Rh(C_6H_5)(diphos)$ (0.40 g, 0.69 mmol) in acetone (20 cm^3), and, after being sealed, the tube was heated at 90 °C (at this temperature the pressure of CO_2 ranged from 2 to 3 atm). The red complex passed slowly into solution, and this became dark red. After 1 h, the solution was cooled to room temperature, the tube was opened, and the solution was filtered and concentrated to about 5 cm^3. Addition of pentane caused precipitation of an orange compound that was filtered, washed with pentane, and dried in vacuo; dec pt >235 °C. Anal. Calcd for $C_{33}H_{29}O_2P_2Rh$: C, 63.67; H, 4.66; P, 9.66. Found: C, 63.9; H, 4.72; P, 9.85. The same complex was obtained by reaction of $Rh(diphos)(BPh_4)$ with CO_2 at 90 °C or else from the reaction of "Rh(diphos)Cl" in benzene with sodium benzoate dissolved in methanol.

Gas Chromatographic Analyses. Methyl benzoate was obtained by the reaction of $Rh(OOC–C_6H_5)(diphos)$ with dry HCl in CH_3OH and subsequent addition of BF_3/CH_3OH. The ester was identified by using a 2-m Carbowax 400 column: 3-mm i.d.; T = 110 °C; carrier N_2, 40 cm^3 min^{-1}.

The products of acetone dimerization were identified by VPC by using the same column as above or else a cyanosilicone 2-m column: T = 150 °C; carrier N_2, 30 cm^3 min^{-1}.

Results and Discussion

A yellow complex that analyzes as $Rh(C_2H_4)(diphos)Cl$ (I) can be obtained from the reaction of $[Rh(C_2H_4)_2Cl]_2$ with the ligand diphos in toluene under nitrogen. Its IR spectrum in Nujol shows a band at 1213 cm^{-1} assigned to the coordinated ethylene[5] and a band at 260 cm^{-1} (ν(Rh–Cl)). Ethylene is released when I is dissolved in $CDCl_3$ or CD_2Cl_2, and, thus, the ^1H NMR spectrum does not show signals of the coordinated ethylene. If I is not isolated once formed, ethylene is slowly released, and an orange solution is obtained which contains the solvated complex "Rh(diphos)Cl".[6] From this solution the dimer $[Rh(diphos)Cl]_2$ slowly separates. Exposure of a benzene solution of "Rh(diphos)Cl" to CO_2 (2 atm) causes a slight color fading, and a strong band at 1712 cm^{-1} (1680 cm^{-1} under $^{13}CO_2$) appears in the IR spectrum of the solution. This band disappears on pumping the cooled solution in vacuo and appears again on exposure of the solution to CO_2. We attribute this band to carbon dioxide coordinated to Rh(I) presumably in the complex $Rh(CO_2)(diphos)Cl$ (II). Attempts to isolate the solid complex (II) failed, and only the dimer $Rh_2(diphos)_2Cl_2$ was obtained.

Table I. Summary of Crystal and X-ray Experimental Data[a]

compd: Rh(diphos)(η-BPh_4) orange triclinic crystals
formula: $C_{50}H_{44}BP_2Rh$ space group $P\bar{1}$
fw: 821

cell parameters: a = 13.698 (5) Å, b = 12.971 (6) Å, c = 12.346 (6) Å, α = 70.81 (3)°, β = 97.31 (4)°, γ = 107.51 (3)°, V = 1989 $Å^3$, Z = 2, d_{calcd} = 1.370 g cm^{-3}, d_{exptl} = 1.372 g cm^{-3}, μ(Mo Kα) = 5.36 cm^{-1}

[a] Data were collected on a Siemens-Hoppe four-circle diffractometer in a 2θ range 7–50° with graphite-monochromatized Mo Kα radiation and the ω-scan technique. The structure has been refined by block-matrix least squares on the basis of 5451 independent reflections, corrected for Lorentz and polarization effects, having $I \geqslant 4\sigma(I)$ (based on counting statistics). Anisotropic temperature factors have been assigned to atoms Rh, P(1), P(2), C(1), C(2), B, and C(11)–C(16), while the phosphine phenyl rings have been constrained into the D_{6h} geometry (C–C = 1.392 Å). The contribution of hydrogen atoms has been kept fixed, and $\Delta f'$ and $\Delta f''$ for Rh and P have been taken into account. This refinement has led to conventional discrepancy indexes of R = 0.047 and R_w = 0.061. More complete experimental details, together with the final atomic coordinates and a listing of F_o/F_c values, are available as supplementary material.

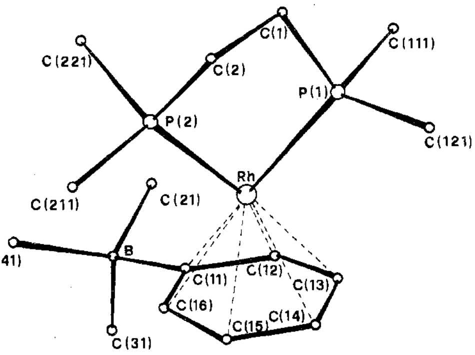

Figure 1. Molecular geometry of the complex Rh(diphos)(η-BPh_4).

The lability of CO_2 in complex II can be explained on the basis of the weak basicity of the substrate "Rh(diphos)Cl", in which the Rh(I) atom is strongly engaged in π back-bonding to the phosphorus ligand, and, thus, the Rh–CO_2 bond presents only a low π bonding character, making the CO_2 weakly bonded.

The solution of the CO_2 complex II is very air sensitive, and in the presence of traces of oxygen a tan solid, poorly soluble in common solvents, precipitates. Its IR spectrum in Nujol shows broad bands at 1660 and 1620 cm^{-1} but no bands attributable to a peroxo group.

Treatment of the solid with iodine at 150 °C affords 0.4 mol of CO_2/mol of complex, but acidolysis with concentrated H_2SO_4 at room temperature affords 0.9 mol of CO_2/mol of complex. On the basis of these features and of elemental

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(5) H. Hiraishi, *Spectrochim. Acta, Part A*, **25**, 1657 (1969).

(6) The complex "Rh(diphos)Cl" has been proposed to be formed in solution, for example, from the reaction of $[Rh(1,5\text{-}COD)Cl]_2$ with diphos, but not isolated: K. Itoh, I. Matsuda, F. Ueda, Y. Ishii, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2118 (1977). Our attempts to isolate the monomer always gave the dimer complex $[Rh(diphos)Cl]_2$.

Table II. Bond Distances (Å) and Angles (Deg) with Their Estimated Standard Deviations

Distances

Rh–P(1)	2.225 (1)	Rh–C(13)	2.279 (5)
Rh–P(2)	2.217 (1)	Rh–C(14)	2.332 (4)
Rh–C(11)	2.441 (4)	Rh–C(15)	2.315 (5)
Rh–C(12)	2.366 (5)	Rh–C(16)	2.283 (4)
C(11)–C(12)	1.405 (7)	C(15)–C(16)	1.423 (6)
C(11)–C(16)	1.420 (8)	C(1)–C(2)	1.523 (9)
C(12)–C(13)	1.419 (6)	C(11)···C(14)	2.894 (6)
C(13)–C(14)	1.405 (9)	C(12)···C(15)	2.812 (8)
C(14)–C(15)	1.407 (8)	C(13)···C(16)	2.762 (7)
B–C(11)	1.658 (6)	B–C(31)	1.650 (7)
B–C(21)	1.653 (9)	B–C(41)	1.656 (7)
P(1)···P(2)	2.982 (2)	P(1)–C(121)	1.843 (3)
P(1)–C(1)	1.849 (5)	P(2)–C(211)	1.818 (5)
P(2)–C(2)	1.845 (5)	P(2)–C(221)	1.842 (3)
P(1)–C(111)	1.838 (5)		

Angles

P(1)–Rh–P(2)	84.3 (0)	P(2)–Rh–C(16)	100.4 (1)
P(1)–Rh–C(13)	100.6 (1)	P(2)–Rh–C(13)	173.7 (2)
P(1)–Rh–C(16)	174.6 (1)	C(13)–Rh–C(16)	74.5 (2)
C(11)–C(12)–C(13)	122.1 (5)	C(12)–C(11)–C(16)	115.1 (4)
C(12)–C(13)–C(14)	121.2 (5)	C(13)–C(14)–C(15)	118.3 (4)
C(11)–C(16)–C(15)	123.6 (4)	C(14)–C(15)–C(16)	118.9 (5)
B–C(11)–C(14)	166.9 (3)	B–C(11)–C(16)	122.2 (4)
B–C(11)–C(12)	121.9 (5)		

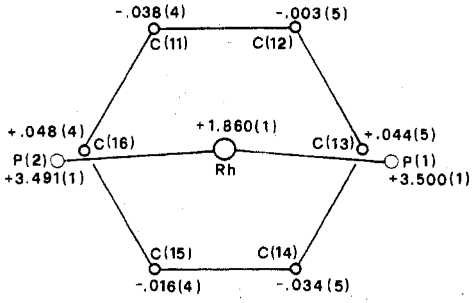

Figure 2. A projection of the inner core of Rh(diphos)(η-BPh_4) on the best plane of the coordinated phenyl ring. Distances from this plane are reported in Å, with esd's in parentheses.

analyses we propose the tan complex to be a carbonate complex of Rh(III).

The reaction of "Rh(diphos)Cl" with $NaBPh_4$ in benzene–ethanol affords the complex Rh(diphos)(BPh_4), a nonconductor in nitrobenzene and acetone and conductor in dimethyl sulfoxide.[7] A crystallographic study has shown that this complex is monomeric with one of the phenyl rings of the tetraphenylborate anion coordinated to the metal. Some experimental features and the principal results of the X-ray work are summarized in Tables I and II and in Figures 1 and 2.

As a result of its interaction with the rhodium atom, the coordinated phenyl ring is not planar (while the remaining three rings of the anion are planar within 3 esd's) but assumes a distorted boat conformation, with two carbon atoms closer to the metal (see Figures 1 and 2). In addition, the mean C–C bond length in this ring is 1.413 Å, vs. an average value of 1.396 Å in the other rings. As can be seen in Figure 2, the set of atoms P(1), P(2), C(13), and C(16) is rigorously planar (with the Rh atom displaced 0.060 Å toward C(11) and C(12)), and their plane forms a dihedral angle of 85.6° with the mean plane of the coordinated phenyl ring. In our opinion, the phenyl distortion is conveniently described in terms of a partially localized covalent bond of Rh to the C(13) and C(16) carbon atoms induced by the presence of the chelating phosphorus ligand and by the tendency of the d^8 Rh(I) to achieve a square-planar coordination. It is worth noting that in Rh[P(OMe)$_3$]$_2$(BPh_4), the only other Rh(I) complex containing the coordinated tetraphenylborate anion for which the structure has been determined,[8] the coordinated phenyl ring presents four carbon atoms, nearly equidistant, at 2.31 Å and two carbon atoms at ca. 2.40 Å; i.e., the phenyl ring presents a boat conformation inverted with respect to that found in the complex described by us. The difference can be explained considering that in the case of Rh[P(OMe)$_3$]$_2$(BPh_4) the plane of the atoms Rh, P(1), and P(2), while still being approximately normal to the mean plane of the coordinated phenyl ring, roughly bisects two opposite C–C edges. As a result, the four carbon atoms at the end of these edges are attracted toward the metal, thus confirming the enhanced ability of Rh(I) to withdraw electron density in the plane of the other two ligands. The different orientation of the coordinated phenyl ring with respect to the Rh, P(1), P(2) plane, observed in the two complexes, suggests that this structural feature is probably determined by packing forces in the solid state.

Halpern[9] has recently described Rh(diphos)(BF_4), containing in the solid state the dimer cation $Rh_2(diphos)_2^{2+}$ in which the two moieties Rh(diphos)$^+$ are bridged by two phenyl rings, one from each of the phosphorus ligands. The complex Rh(diphos)(η-BPh_4) (III) coordinates CO_2 at room temperature in CH_2Cl_2 at pressures higher than 10 atm, affording a solution whose IR spectrum shows a band at 1722 cm^{-1} (1685 cm^{-1} under $^{13}CO_2$). CO_2 is released easily at lower pressure, and the starting complex is also recovered unaltered from the pressurized CH_2Cl_2 solution added with benzene. When heated in acetone under CO_2, III converts into a new orange complex which shows IR bands at 1597 (mw), 1550 (ms), and 1380 (ms) cm^{-1} (Nujol mull). The analyses of the compound agree with the formula Rh(OOC–C_6H_5)(diphos). To gain an insight into the mechanism of this reaction we have heated complex III in acetone under N_2 or CO_2 under controlled conditions. At $T \simeq 70$ °C the light orange complex III converts into Rh(C_6H_5)(diphos) (IV) which then reacts with CO_2 to afford Rh(OOC–C_6H_5)(diphos) (V), identical with an authentic sample prepared from "Rh(diphos)Cl" and sodium benzoate. On the basis of its IR spectrum we propose that the benzoate group is bidentate.[10] This CO_2 insertion into the Rh–C bond is similar to that reported by Vol'pin for the complex Rh(C_6H_5)(PPh_3)$_3$.[11] The benzoato complex reacts with HCl and then CH_3OH/BF_3 to afford quantitatively methyl benzoate.

Phenyl migration is a common reaction in organic chemistry[12] and it has been reported for systems such as Ph_3M–Pt(Cl)(PPh_3)$_3$[13] (M = Sn, Pb). A few other examples of phenyl transfer from the anion tetraphenylborate to metals (Hg,[14] Pt,[15] Ru,[16] Ni[17]) have been reported. In the present

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(7) Λ_M = 19 S mol^{-1} cm^2 for a 1.88 × 10^{-3} M solution. For comparison, for a 10^{-3} M solution of a 1:1 electrolyte Λ_M = 37 S mol^{-1} cm^2 in Me_2SO: D. E. Arrington and E. Griswold, *J. Phys. Chem.*, **74**, 124 (1970).

(8) M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Commun.*, 1406 (1969). It is worth noting that in (Cp)Ru(η-BPh_4), which does not require a square-planar geometry, the coordinated phenyl ring is planar: G. J. Kruger, A. L. Du Preez, and P. J. Haines, *J. Chem. Soc., Dalton Trans.*, 1302 (1974).

(9) J. Halpern, D. P. Riley, A. C. S. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8055 (1977).

(10) S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, **11**, 660 (1972).

(11) I. S. Kolomnikov, A. O. Gusev, T. S. Belopotapova, M. Kh. Grigoryan, T. V. Lysyak, Yu. T. Struchkov, and M. E. Vol'pin, *J. Organomet. Chem.*, **69**, C10 (1974).

(12) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry", McGraw-Hill, New York, 1970.

(13) M. C. Baird, *J. Inorg. Nucl. Chem.*, **29**, 367 (1967).

(14) G. E. Coates, "Organometallic Compounds", 2nd ed., Wiley, New York, 1960.

(15) H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **91**, 596 (1969).

(16) R. J. Haines and A. L. Du Preez, *J. Am. Chem. Soc.*, **93**, 2820 (1971).

case the migration is certainly made possible by the coordination of the phenyl ring to the metal. This constitutes the first example of phenyl migration from the anion tetraphenylborate to Rh(I) and represents an interesting route to phenyl–rhodium(I) complexes as the yields are very good (ca. 85%).

Complex IV is monomeric in CH_2Cl_2 but an X-ray structure is necessary in order to ascertain if it can be considered a real tricoordinate complex of Rh(I) in the solid state.[18]

VPC of the acetone solutions from which the phenyl- and the benzoato–rhodium(I) complexes were isolated has shown that Rh(I) catalyzes the dimerization of acetone to mesityl oxide (MO) and diacetone alcohol (DAA). It is of relevance that CO_2 influences the DAA/MO ratio, which is equal to 1 under nitrogen and rises to 4 under CO_2. It is known that CO_2 can influence the catalytic activity of metal complexes.[19] The fact that under CO_2 the amount of DAA (that requires a basic catalyst[20]) is increased with respect to MO is best explained by taking into account the formation of complex V, as the simple interaction of CO_2 with the Rh atom in complex IV would conversely reduce the basicity of the catalyst.

Preliminary studies on the evaluation of the catalytic activities of the complexes Rh(diphos)(η-BPh_4), Rh(C_6H_5)(diphos), and Rh(OOC–C_6H_5)(diphos) seem to support this hypothesis.

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Registry No. I, 72318-20-8; III, 72332-27-5; IV, 72318-21-9; V, 72318-22-0; $[Rh(diphos)Cl]_2$, 53204-14-1; CO_2, 124-38-9; $[Rh(C_2H_4)_2Cl]_2$, 12122-73-5.

Supplementary Material Available: X-ray experimental section, atomic coordinates and thermal parameters (Table III), and calculated and observed structure factors (Table IV) (24 pages). Ordering information is given on any current masthead page.

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(17) L. Sacconi, P. Dapporto, and P. Stoppioni, *Inorg. Chem.*, **15**, 325 (1976).

(18) Rh(I) complexes with the bulky ligand tricyclohexylphosphine of formula $RhX(PCy_3)_2$ (X = F, Cl, Br) are supposed to be tricoordinate in the solid state. These are among the few tricoordinate complexes of Rh(I) isolated in the solid state: H. L. M. Van Gaal and F. L. A. Van den Bekeron, *J. Organomet. Chem.*, **134**, 237 (1977).

(19) (a) J. E. Konhle, L. H. Slaugh, and K. L. Nakamaye, *J. Am. Chem. Soc.*, **91**, 5904 (1969); (b) A. Musco and A. Silvani, *J. Organomet. Chem.*, **88**, C41 (1975).

(20) F. L. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1963.

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Further Work on the Calculation of d-Orbital Energies of Cobalt Porphyrins from Electron Spin Resonance Data

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In a previous study,[1] the deviation of **g** tensors of cobalt porphyrins from the free spin *g* value was correlated with the nonplanarity of the macrocyclic ring. Cobalt tetraphenylporphyrin (TPP) topped the list by having $g_{\|} = 1.798$ and $g_{\perp} = 3.322$. More recently, it was found that cobalt octaethylporphyrin (OEP) doped in NiOEP had even smaller $g_{\|}$ and even larger $g_{\perp}$.[2] It is therefore particularly interesting to note that while, for TPP, the methene carbon atoms are ±0.4 Å from the metal–nitrogen plane (±0.42 Å for CuTPP[3] and ±0.38 Å for H_2TPP[4]), the deviation in the case of NiOEP is even larger, ±0.51 Å.[5]

Table II. Experimental Data

	$g_{\|}$	$g_{\perp}$	$A_{\|}$, cm^{-1}	$A_{\perp}$, cm^{-1}
Co(*p*-COOH)TPP in pyridine (2:1)[8]	2.054	2.236	0.0053	−0.0052
CoTPyP in H_2TPyP[9]	1.774	3.218	0.0213	0.0383
CoOEP in NiOEP[2]	1.599	3.391	0.0195	0.0454

Table III. Calculated Results

V_1	V_2	V_3	$g_{\|}$	$g_{\perp}$	P, cm^{-1}	κ	$K = P\kappa$
Co(*p*-COOH)TPP in Pyridine (2:1 Complex)							
26.5	37.5	28.0	2.053	2.236	0.0170	0.266	0.0045
22.0	33.0	34.0	2.051	2.231	0.0176	0.266	0.0047
18.2	29.2	40.0	2.057	2.235	0.0186	0.262	0.0049
CoTPyP in H_2TPyP							
28.58	27.0	28.0	1.775	3.206	0.0223	−0.567	−0.0127
28.90	27.2	30.3	1.768	3.224	0.0223	−0.555	−0.0124
29.17	27.4	36.0	1.780	3.226	0.0230	−0.511	−0.0117
CoOEP in NiOEP							
29.88	27.6	26.0	1.598	3.400	0.0256	−0.322	−0.0082
30.00	27.7	28.0	1.595	3.397	0.0270	−0.228	−0.0061
30.27	27.9	34.0	1.603	3.402	0.0274	−0.207	−0.0057

In the last study,[1] the **g** tensors of the various cobalt porphyrins were satisfactorily accounted for by using expressions for the ground Kramer states, those obtained from the diagonalization of the matrix of ligand field, electrostatic energy, and spin–orbit coupling.[6] In so doing, it was also possible to deduce the metal d-orbital energies. In the present work, the calculation is extended to include CoOEP. Two further refinements in the calculation are introduced. The first is the inclusion of configuration interaction in the electrostatic energy which was neglected previously. Second, the Kramer doublet which yields the proper **g** tensor is further checked to see if the **A** tensors could simultaneously be satisfied.

The complete energy matrix, including configuration interaction, is given in Table I (supplementary material). The expressions for $g_{\|}$ and $g_{\perp}$[1] are omitted from this paper to avoid repetition. The general expressions for $A_{\|}$ and $A_{\perp}$ are given by Griffith (eq 1 and 2).[7] In these equations, $|+\rangle$ and $|-\rangle$

$$A_{\|} = P[g_{L\|} - {}^1\!/_2\kappa g_{S\|} + {}^2\!/_7\langle +|\sum_k \mathbf{a}_{kz}|+\rangle] \qquad (1)$$

$$A_{\perp} = P[g_{L\perp} - {}^1\!/_2\kappa g_{S\perp} + {}^1\!/_7\langle -|\sum_k \mathbf{a}_{\bar{k}}|+\rangle] \qquad (2)$$

stand for the Kramer doublet. The vector, $\mathbf{a}_k = 4\mathbf{s}_k - (\mathbf{l}_k\cdot\mathbf{s}_k)\mathbf{l}_k - \mathbf{l}_k(\mathbf{l}_k\cdot\mathbf{s}_k)$, and the matrix elements of the components, a_z and $a = a_x - ia_y$, can be found in Griffith's table 41.[7] If the Kramer doublet is determined, eq 1 and 2 can be used to solve for the parameters P and κ. κ is a measure of the isotropic contribution to the hyperfine coupling and P, as shown above, implicitly includes the "orbital reduction" factor, hence giving some information about the delocalization of the unpaired electron.

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(1) W. C. Lin, *Inorg. Chem.*, **15**, 1114 (1976); "The Porphyrins", Vol IV, D. Dolphin, Ed., Academic Press, New York, 1979, p 373.

(2) D. Dolphin and T. Takui, unpublished result from this department.

(3) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 1353 (1963).

(4) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Am. Chem. Soc.*, **85**, 2334 (1963).

(5) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **28**, 2162 (1972).

(6) For earlier similar type calculations see L. M. Engelhardt and M. Green, *J. Chem. Soc., Dalton Trans.*, 724 (1972); C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *ibid.*, 754 (1973).

(7) J. S. Griffith, "The Theory of Transition-Metal Ions", Cambridge University Press, New York, 1961, pp 328, 343, 427.

(8) W. C. Lin and P. W. Lau, *J. Am. Chem. Soc.*, **98**, 1447 (1976).

(9) P. W. Lau and W. C. Lin, *J. Inorg. Nucl. Chem.*, **37**, 2389 (1975).