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)$_2$Cl]$_2$, 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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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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Since the present calculation differs a little from the previous, two of the complexes (Co(*p*-COOH)TPP in pyridine and CoTPyP in H_2TPyP) treated before are recalculated here for direct comparison. The set of orbital energies, V_1, V_2, and V_3 ($V_1 = E(b_1) - E(a_1)$, $V_2 = E(b_1) - E(e)$, $V_3 = E(b_1) - E(b_2)$), which yield acceptable *g* values are found to be not entirely unique. However, the values vary within finite ranges, and three representative calculations for each system are shown here in order to cover the allowed variations. The experimental data are given in Table II and the calculated data in Table III.

As can be seen from Table III, for unsolvated complexes CoTPyP and CoOEP, the allowed variations in V_1 and V_2 are not large. The variation in V_3 is appreciable and indicates that the method is not sensitive enough to evaluate V_3 accurately. For the case of solvent coordinated complex, although the variations in V_1 and V_2 are quite appreciable when viewed separately, the difference, $V_2 - V_1$ (i.e., $E(a_1) - E(e)$), however does not vary. This shows that $g_\parallel$ and $g_\perp$ are very sensitive to a change in $(V_2 - V_1)$. In all cases however, the values of P and κ are seen to be insensitive toward variations in V_i. The values of K ($=P\kappa$) calculated previously by the perturbation method for CoTPyP and the (2:1) solvent-coordinated complex were −0.0125 and 0.0043, respectively.[10] These compare fairly well with the present figures. The value of P for CoOEP is very nearly the free-ion value of 0.0254 while that for CoTPyP is slightly lower. The much lower value of $P = 0.018$ for the solvated complex is in agreement with the fact that the unpaired electron is delocalized through σ bonding from the Co d_{z^2} orbital to the nitrogen orbitals of the two solvent molecules.

In concluding this note, it must be mentioned that although in previous calculations[1] which neglected the configuration interaction, the values of V_3 were found to be much smaller, all the conclusions drawn in that study are still valid nevertheless. For instance, the excited state $^4B_2$ is still found to be coupled to the ground state $^2A_1$ to a large extent in unsolvated cobalt porphyrins.

Appendix

When the Kramer doublet, $|+\rangle, |-\rangle$, is expressed as

$$|+\rangle = \sum_{i=0}^{15} \eta_i |\psi_i\rangle \qquad |-\rangle = \sum_{i=0}^{15} \eta_i |\psi_i'\rangle$$

with $|\psi_i\rangle, |\psi_i'\rangle$ defined as before,[1] the matrix elements $\langle +|\sum_k a_{kz}|+\rangle$ and $\langle -|\sum_k a_k^-|+\rangle$ in eq 1 and 2 turn out to be as follows:

$$\begin{aligned}\langle +|\sum_k a_{kz}|+\rangle = {} & 2\eta_0^2 - \eta_1^2 + \eta_2^2 + 3\eta_3^2 + \eta_4^2 - 5\eta_5^2 - 6\eta_6^2 \\ & + 2(\eta_7^2 + \eta_8^2 - \eta_9^2 - \eta_{10}^2) - 3\eta_{12}^2 + 5\eta_{13}^2 - \eta_{14}^2 - \\ & \eta_{15}^2 - \sqrt{6}\eta_0\eta_1 - 3\sqrt{2}\eta_0(\eta_2 + \eta_3) - 3\sqrt{2}\eta_1(\eta_9 - \eta_{11}) - \\ & \sqrt{6}(\eta_2\eta_9 - \eta_3\eta_{11} + \eta_5\eta_{10} - \eta_6\eta_{12} + \eta_7\eta_{15} + \eta_8\eta_{14})\end{aligned}$$

$$\begin{aligned}\langle -|\sum_k a_{k}^-|+\rangle = {} & -2\eta_0^2 - 6\eta_1^2 + \\ & \sqrt{6}(\eta_0\eta_1 + \eta_2\eta_{11} - \eta_3\eta_9 - \eta_4\eta_9 - \eta_6\eta_{13} + \eta_7\eta_{14} + \eta_8\eta_{15}) - \\ & 3\sqrt{2}(\eta_0\eta_4 + \eta_0\eta_5 - \eta_1\eta_{10}) - 4\sqrt{3}\eta_1\eta_4 + \\ & 4(\eta_2\eta_3 - \eta_2\eta_5 + \eta_6\eta_7 + \eta_6\eta_8 - \eta_7\eta_8 + \eta_7\eta_{10} + \eta_{12}\eta_{14} + \\ & \eta_{12}\eta_{15}) + 2(\eta_2\eta_4 - \eta_{12}\eta_{13}) - 12(\eta_9\eta_{11} + \eta_{14}\eta_{15})\end{aligned}$$

Registry No. Co(*p*-COOH)TPP(py)$_2$, 58512-42-8; CoTPyP, 14244-55-4; CoOEP, 17632-19-8.

Supplementary Material Available: Table I showing the energy matrix (1 page). Ordering information is given on any current masthead page.

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Aspects of the Low-Temperature Chemistry of Tris(triphenylphosphine)platinum(0)

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A distinctive feature of the chemistry of platinum(0) phosphine and related d^{10} complexes is the accessibility of a range of stable coordination numbers.[1,2] This is reflected in the occurrence of stable complexes with coordination numbers ranging from 2 to 4, e.g., $[Pt(P(i\text{-}Pr)_3)_2]$,[3] $[Pt(PPh_3)_3]$,[4] and $[Pt(PEt_3)_4]$[5] (the preferred coordination number being influenced by both steric and electronic factors)[6] and in the duality of mechanisms exhibited, for example, by $[Pt(PPh_3)_3]$, which has been shown to undergo substitution and oxidative addition reactions simultaneously by associative and dissociative mechanisms.[7,8]

In some instances Pt(0) combines with a given ligand to form two or more stable complexes with different coordination numbers. Thus, $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$ are both stable compounds in the solid state.[4] However, $[Pt(PPh_3)_4]$ has been reported[9] to dissociate completely (to $[Pt(PPh_3)_3]$ and PPh_3) in solvents such as benzene or toluene. (Although kinetic evidence supports a dissociative mechanism for certain substitution reactions of $[Pt(PPh_3)_3]$,[7,10] $[Pt(PPh_3)_2]$ does not appear to have been identified or characterized in solution.[11]) Virtually all reported studies pertaining to the association–dissociation and substitution reactions of $[Pt(PPh_3)_3]$ in solution have been conducted at ambient temperatures. We now report the extension of such studies to lower temperatures (down to −100 °C) where we have found the solution chemistry of $[Pt(PPh_3)_3]$ to be significantly different from that at room temperature. Of pertinent interest is one prior investigation involving the closely related $[Pt(P(p\text{-}C_6H_4CH_3)_3)_n]$ system.[13]

Reaction with PPh_3. At room temperature only a very broad ^{31}P NMR signal was observed for a toluene solution of $[Pt(PPh_3)_3]$. When the solution was cooled to −70 °C, the resonances sharpened to give the characteristic line due to $[Pt(PPh_3)_3]$ (δ 49.9) together with two ^{195}Pt satellites ($J_{Pt-P} = 4438$ Hz; see Table I). Addition of 0.5 equiv of PPh_3 to this solution resulted in broadening of the NMR signal. However, further cooling of the solution to −100 °C caused the spectrum to sharpen, revealing two signals assignable to $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$, respectively (see Figure 1 and Table I). No signal due to free PPh_3 could be detected. Thus, it is concluded that

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[11] The isolation of solid "$[Pt(PPh_3)_2]$" and examination of some of the chemistry of this substance in solution have been claimed.[12] However, subsequent attempts to prepare $[Pt(PPh_3)_2]$ *in monomeric form* under conditions where it is sufficiently stable for direct detection and characterization, either in solution or as a solid, appear to have been unsuccessful.

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