Inorg. Chem. **1987**, *26*, 1449–1451 **1449**

Using in (2) the experimental Δg's, we can estimate the $J_{e,e',g}$ integrals from the D^{ex}_{ij} (i ≠ j) elements. This procedure gives

$$J_{xz,yz,xy} = -0.2\ (1.3) \qquad J_{xz,x^2-y^2,xy} = 0.3\ (-3) \qquad J_{yz,x^2-y^2,xy} = -0.1\ (-0.4) \tag{3}$$

expressed in cm^{-1}. The values in parentheses in (3) refer to $\mathbf{D}^{ex}_2$. Extracting the $J_{e,e',g}$ integrals from the diagonal elements of $\mathbf{D}^{ex}$ is complicated by the fact that the experimental **D** tensor is traceless and the three principal values are not linearly independent. Assuming an overall C_{2h} symmetry for the dinuclear complex, the four HOMO's of the oxalato molecule[35] span the $A_u + A_g + B_u + B_g$ irreducible representations of the C_{2h} point group (Figure 5). The $|xy\rangle$ and $|yz\rangle$ orbitals on copper span $a_u + b_g$, and $|x^2 - y^2\rangle$ and $|xz\rangle$ span $a_g + b_u$. $J_{yz,yz,xy}$ is expected to be antiferromagnetic (positive sign) due to antiferromagnetic exchange pathways of the type $xy\|(A_u + B_g)\|yz$, and a ferromagnetic value (negative sign) is anticipated for $J_{xz,xz,xy}$ and $J_{x^2-y^2,x^2-y^2,xy}$ through the exchange pathways $xy\|(A_u + B_g) \perp (A_g + B_u)\|xz,x^2 - y^2$. This leads in (2) to $D^{ex}_{xx} < 0$, $D^{ex}_{yy} > 0$, and $D^{ex}_{zz} < 0$.

By making (2) traceless, we obtain the diagonal elements of the $\mathbf{D}^{e}$ tensor to compare with $\mathbf{D}^{ex}_1$ and $\mathbf{D}^{ex}_2$:

$$D^{e}_{xx} = (2D^{ex}_{xx})/3 - D^{ex}_{yy}/3 - D^{ex}_{zz}/3 \tag{4}$$

$$D^{e}_{yy} = (2D^{ex}_{yy})/3 - D^{ex}_{xx}/3 - D^{ex}_{zz}/3 \tag{5}$$

$$D^{e}_{zz} = (2D^{ex}_{zz})/3 - D^{ex}_{xx}/3 - D^{ex}_{yy}/3 \tag{6}$$

Using the signs anticipated for D^{ex}_{ii}, eq 5 requires that $D^{e}_{yy} > 0$. This condition is matched only by the $\mathbf{D}^{ex}_1$ tensor.

Since (4)–(6) are not linearly independent, it is not possible to uniquely determine D^{ex}_{ii} from the experiment. In series of copper(II) dimers formed by square-planar monomeric units, it was usually found[6,8] that, to a good approximation, $J_{xz,xz,xy} = J_{yz,yz,xy} = 0$ and a ferromagnetic value was measured for $J_{x^2-y^2,x^2-y^2,xy}$. In the present case eq 4 and 5 would require $D^{e}_{xx} = D^{e}_{yy} = -D^{e}_{zz}/3$, which is not observed for either $\mathbf{D}^{ex}_1$ or $\mathbf{D}^{ex}_2$, and we must expect $J_{xz,xz,xy} \neq J_{yz,yz,xy} \neq 0$. This is probably due to the deviation of the copper from the coordination plane observed in the present complex, which lowers the symmetry of the copper coordination environment and is expected to increase the overlap density between the $|xy\rangle$, $|xz\rangle$, and $|yz\rangle$ type molecular orbitals since the $|xy\rangle$ molecular orbital is no longer in a nodal plane of the other two orbitals. In order to estimate, however, the order of magnitude of the exchange interaction, we put in (6) $D^{ex}_{xx} = D^{ex}_{yy} = 0$. By equating (6) to $D^{ex}_{1,zz}$, we get $J_{x^2-y^2,x^2-y^2,xy} = -10$ cm^{-1}.

Conclusions

It is definitely clear that anisotropic exchange interactions are operative in determining the zero-field splitting of exchange-coupled copper(II) complexes. These interactions decrease drastically on increasing the complexity of the molecular groups bridging the two metals from values around 200–300 cm^{-1} for monoatomic bridges[6] to 50 cm^{-1} for N_3^- bridges[9] and 10–30 cm^{-1} for triazoles[10] and oxalates, and EPR spectroscopy is a very sensitive and useful tool to investigate these interactions. This behavior can be qualitatively understood on the basis of density overlap considerations, which demand a decrease of the overlap density on passing from monoatomic to extended bridges, while a quantitative model allowing for an accurate description of the interaction is still lacking. The present results show that even with bridges as extended as the oxalato ones exchange contributions to **D** cannot be neglected and, even if they do not cause significant deviations of the absolute value of D from the value arising from the magnetic dipolar interaction, low-symmetry effects can yield largely misaligned **g** and **D** tensors.

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Registry No. $[Cu_2(phen)_2(C_2O_4)(NO_3)_2]$, 106762-40-7.

Supplementary Material Available: Tables of thermal parameters (Table SI) and positional parameters of the hydrogen atoms (Table SII) (2 pages); a table of observed and calculated structure factors (Table SIII) (13 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Institut für Anorganische Chemie
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Synthesis and Crystal Structure of $[Re(bpy)_3](ReO_4)_2$ (bpy = 2,2′-Bipyridine)

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The complexes $Ru(bpy)_3^{2+}$ and $Re(bpy)(CO)_3Cl$ and related compounds are widely used as photosensitizers and/or catalysts for the conversion of light into chemical energy.[2] This and the scarcity of structurally characterized mononuclear octahedral Re(II) complexes[3] prompted us to report the synthesis, crystal structure, and some physical properties of air-stable $[Re(bpy)_3](ReO_4)_2$ (**1**), which may serve as a starting material for $Re(bpy)_3^+$, an isoelectronic analogue of $Ru(bpy)_3^{2+}$.

Synthesis

1 was synthesized under a nitrogen atmosphere; 378 mg (1.0 mmol) of K_2ReF_6 was added to a hot solution (85 °C) of 487 mg (3.0 mmol) of 2,2′-bypyridine in 50 mL of H_2O. The resulting clear pink solution was kept at 85 °C for 48 h. During this time the color slowly changed to dark purple. The reaction mixture was then cooled to room temperature, and placed in a refrigerator. Air-stable blue-black, hexagonal prismatic crystals formed, which were collected by filtration, washed with ice–cold water and cold ethanol, and finally dried with ether (yield 30%).

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(1) (a) Institut für Anorganische Chemie. (b) Laboratorium für Kristallographie.

(2) See: Balzani, V.; Bolletta, F. *Comments Inorg. Chem.* **1983**, *2*, 211. Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984. Hawecker, J.; Lehn, J. M.; Ziessel, R. *J. Chem. Soc., Chemm. Commun.* **1983**, 536.

(3) A search through the Cambridge Crystallographic Data File revealed the structure of four mononuclear octahedral Re(II) compounds.[16–18]

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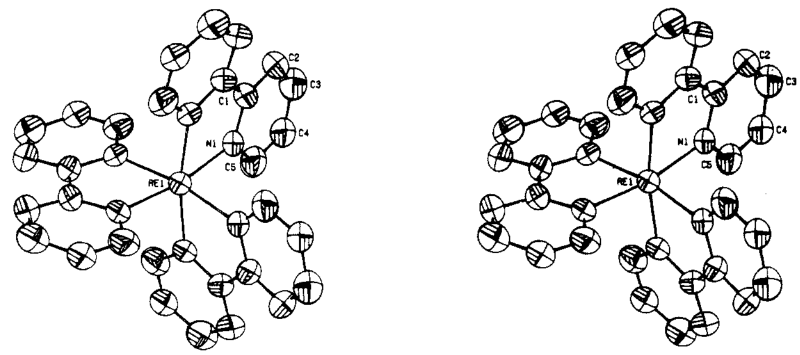

Figure 1. ORTEP stereoscopic view of $[Re^{II}bpy_3]^{2+}$ showing atomic labeling. $d(Re1-N1) = 2.094\ (8)$, $d(N1-C1) = 1.36\ (1)$, $d(C1-C2) = 1.36\ (1)$, $d(C1-C1') = 1.48\ (2)$, $d(C2-C3) = 1.44\ (2)$, $d(C3-C4) = 1.38\ (2)$, $d(C4-C5) = 1.36\ (1)$, $d(N1-C5) = 1.41\ (2)$ Å; $\angle(N1-Re1-N1a) = 76.5$, $\angle(N1-Re1-N1b) = 91.4$, $\angle(N1-Re1-N1c) = 96.4$, $\angle(N1-Re1-N1d) = 170.0°$.

Physical Properties

Chemical analysis and spectral data of **1** are in accord with the chemical composition $[Re(bpy)_3](ReO_4)_2 \cdot H_2O$.[4] The magnetic data show Curie behavior between 2 and 70 K, with an average magnetic moment of 1.61 (1) μ_B (corrected for diamagnetic contributions).[6] The average magnetic moment agrees well with those reported for other Re(II) compounds,[6] although it does not exclude the possibility of Re(III).[7] The UV-vis spectrum in water shows maxima at 495 (ϵ = 1880), 375 (2500), and 302 (14200) nm. The spectrum of $Os(bpy)_3^{3+}$ in 3 M HCl shows absorption at 563 (ϵ = 585) 428 and 458 (< 100), and 307 and 316 ($\approx$40000 nm).[9] The absorption at ~300 nm has been found in a number of related complexes and is generally attributed to a ligand $\pi \rightarrow \pi^*$ transition. The other two transitions in **1** are shifted by about 70 nm to higher energies compared to those in $Os(bpy)_3^{3+}$. this is not in disagreement with assigning one of the two as a lignd-to-metal $\pi \rightarrow t_2$ charge transfer. Such a transition is expected to occur at higher energies for decreasing charge and atomic number of the metal ion. No emission spectrum was taken.

Structure Determination

The clearest evidence for the identity of **1** comes from a single crystal X-ray diffraction experiment. A crystal with the dimensions of 0.23 × 0.13 × 0.20 mm was used. Crystal data for $[Re(bpy)_3](ReO_4)_2$: M_r : 1155.2, $P\bar{3}c1$, a = 10.550 (3) Å, c = 16.432 (6) Å, V = 1584(2) Å^3, Z = 2, D_{measd} (flotation) = 2.42 (2) g cm^{-3}, D_{calcd} = 2.422 g cm^{-3}, (graphite monochromator, Mo Kα) λ = 0.71069 Å, μ = 116.5 cm^{-1}, $F(000)$ = 1070, T = 295 K, $2\theta \leq 50°$, 2507 reflections measured, 721 unique reflections with $I \geq 2\sigma(I)$ used (octants $h,k,\pm l$; agreement factor for observed and accepted F_0 0.020). Data were collected with a CAD4 diffractometer (Enraf-Nonius), data reduction was performed with SDP,[10] and least-squares refinement was done with SHELX76.[11] Numerical absorption correction were applied with SDP, maximum and minimum transmission factors of 0.162 and 0.100. Neutral-atom scattering factors were corrected for real and imaginary anomalous dispersion.[12] $[Re(bpy)_3](ReO_4)_2$ is isomorphic with $[Ru^{II}(bpy)_3](PR_6)_2$[13] implying D_3 site symmetry for the complex cation and C_3 symmetry for the anions. This is confirmed by the structure analysis. Refinement of anisotropic Re, C, N, and O led to R = 0.048. The U_{33} values of the cation's atoms (Re1, C, and N) were all ~0.1 Å^2, significantly larger than corresponding U_{11} values. For Re2 the reverse was observed. A difference Fourier shows 2.7 e Å^{-3} of residual electron density along the 3-fold axis above and below Re1 and 1.5 e Å^{-3} off the 3-fold axis in the neighborhood of Re2. These observations may be interepreted in terms of disorder and modeled by allowing the cation to move along the C_3 axis above and below the C_2 axis of the D_3 symmetric site (occupation $^1/_2$); similarly, the anion is allowed to move off the C_3 axis (occupation $^1/_3$).[14] Split atoms were introduced into refinement for Re1, Re2, and O2 but, due to comparatively low scattering power, not for C and N. Site symmetry constraints on the displacement parameters were relaxed for O2 but not for Re2. This ensures convergence of the least-squares refinement to R = 0.031 (Table I). The largest features in the final difference Fourier map are .+0.66 (~0.92 Å from Re2) and −0.68 e Å^{-3}. In the second model, Re1 is displaced by z = 0.212 (3) Å from the C_2 axis and U_{33} decreased from 0.1090 (9) Å^2 to 0.0542 (19) Å^2. The difference of 0.0548 (21) Å^2 is well accounted for by z^2 = 0.0449 (13) Å^2. Since U_{33} values for the unsplit N and C atoms in the second model remain at about 0.1 Å^2 it seems reasonable to assume the same disorder for all three atom types and to calculate bond distances and bond angles and their esd's from mean (unsplit) positions.[15]

Table I. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1** (Split Atom Model)

atom	x/a	y/b	z/c	B_{eq}, Å^2
Re1	0.0000 (0)	0.0000 (0)	0.2629 (2)	3.42 (3)
Re2	0.3154 (8)	0.6596 (18)	0.1407 (0)	4.34 (5)
N1	0.1963 (8)	0.1154 (10)	0.1852 (6)	5.11 (19)
C1	0.2943 (11)	0.2526 (11)	0.2113 (6)	4.77 (25)
C2	0.4182 (12)	0.3435 (12)	0.1699 (8)	5.96 (29)
C3	0.4457 (14)	0.2915 (15)	0.0949 (8)	6.38 (36)
C4	0.3520 (12)	0.1493 (12)	0.0702 (7)	5.65 (29)
C5	0.2292 (12)	0.0634 (13)	0.1141 (7)	5.61 (28)
O1	0.1966 (13)	0.5043 (13)	0.1708 (9)	15.12 (51)
O2	0.3451 (208)	0.6237 (113)	0.0484 (14)	27.5 (36)

[a] $B_{eq} = {}^8/_3\, \pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} - U_{12}hka^*b^*)$.

The disorder might be related to a structural phase transition observed to begin at ~−30 °C. When the crystal was cooled, a broadening of the reflections chosen to check the orientation matrix

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[4] Anal. Calcd for $[Re(bpy)_3](ReO_4)_2 \cdot H_2O$: Re, 47.61; C, 30.71; H, 2.23; N, 7.16; H_2O, 1.54. Found: Re, 48.83; C, 29.95; H, 2.37; N, 6.99; H_2O, 1.81.[5] IR (KBr): 3400, 3050, 1605, 1582, 1465, 1440, 1415, 1245, 1005, 1000, 915, 765, 725, 655, 325, 300, cm^{-1}.

[5] The crystal structure analysis did not show a water molecule in the crystal lattice.

[6] Landolt-Börnstein *Physykalische und Chemische Tabellen*; Springer-Verlag: West Berlin, 1976, Neue Serie II, Vol. 2, 8, 10, 11.

[7] A compound said to be $[Re^{III}(bpy)_3]^{3+}$ has been reported.[8] Its magnetic moment of 1.0 μ_B at room temperature does not seem to be compatible with known magnetic moments of mononuclear octahedral Re(III) complexes.[6] No other proof for the composition of this compound was given.

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[14] An attempt to solve the structure in a lower space group ($P\bar{3}$) led to higher R values.

[15] Combining the split positions of Re1 with the average positions of N and C leads to a distorted octahedral complex with three symmetry-related Re–N distances of ~1.7 Å and three others of ~2.5 Å, chemically most unlikely. Similar arguments hold for the anion. Mean positions: for Re1, 0.0, 0.0, 0.25; for Re2, 0.3333, 0.6667, 0.1407; for O2, 0.3333, 0.6667, 0.0484.

was noticed. Eventually the reflections became too broad to be measured. When the crystal was allowed to warm up, the reflection profiles narrowed again but showed about 10% loss of intensity. The process could be repeated through several cycles with less intensity loss each time.

Re(II) shows a roughly octahedral coordination geometry with dimensions very similar to those of $[Ru(bpy)_3]^{2+}$ (Figure 1; *d*(Ru–N) = 2.06 Å). There are only four other mononuclear octahedral Re(II) complexes available for comparison: $[Re^{II}(NO)Br_4(CH_3CH_2O)][N(CH_2CH_3)_4]$[16] (**2**), $[Re^{II}(NO)Cl_4(C_5H_5N)][N(CH_2CH_3)_4]$[17] (**3**), $[Re^{II}(NO)Br_4(CH_3CN)][N(CH_2CH_3)_4]$[16] (**4**), and $[Re^{II}(CNC(CH_3)_3)_2(CH_3CCN)][N(CH_2CH_3)_4]$[16] (**4**), and $[Re^{II}(CNC(CH_3)_3)_2(CH_3CN)_2(P(C_6H_5)_3)_2](BF_4)$[18] (**5**). The Re–NO distances in **2**–**4** are 1.72, 1.75, and 1.77 Å, respectively. The Re–N (pyridine) distance in **3** is 2.22 Å and the $Re–NCCH_3$ distance in **4** is 2.14 Å, both of which are trans to an NO ligand. In **5** the trans $Re–NCCH_3$ distances are 2.055 and 2.058 Å, which compare very well with the observed Re–N distance of 2.09 Å in **1**. Re–N distances of three octahedral Re(V) and one octahedral Re(I) compounds with ethylenediamine, bpy, and pyridine as ligands are all about 2.15 Å.[19] The observed Re2–O1 and Re2–O2 distances are 1.67 and 1.61 Å, respectively, both shorter than the 1.72 Å observed for $KReO_4$.[20] The shortening is probably due to disorder.

Acknowledgment. A.G. is grateful to the Swiss National Science Foundation for a postdoctoral fellowship.

Supplementary Material Available: Listings of displacement parameters, bond lengths and angles, and magnetic data and a figure depicting the UV-vis spectrum for **1** (3 pages); a listing of structure factors for **1** (5 pages). Ordering information is given on any current masthead page.

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Study of the Reactivity of the Single-Chloro-Bridged Dissymmetric Dinuclear Rhodium Species $(CO)_2(Cl)Rh(\mu\text{-}Cl)Rh(CO)[PhP(OC(CH_3)_2CH_2)_2NH]$

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The reaction of $[Rh(CO)_2Cl]_2$ with bicyclic amino phosphorane ligands in the Rh/ligand ratio 2/1 was shown to lead to the unusual single-chloro-bridged Rh_2 complex **1**.[1]

The novel characteristics of **1** lie in its having a single bridging chlorine atom between the two metal atoms, which are both in a formal oxidation state of I, and the nonsymmetric substitution of the two Rh atoms, whose actual charges are therefore different.

Complex **1** was expected to exhibit considerable reactivity, especially toward nucleophiles and small unsaturated molecules. We report here our investigations, whose results are summarized in Scheme I.

Experimental Section

Melting points were determined with a Reichert microscope in sealed capillaries. Elemental analyses were performed by the Centre de Microanalyses du CNRS. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer, ^1H, ^{31}P, and ^{19}F NMR spectra on a Bruker WH-90 or a Bruker 80 instrument, and ^{13}C and natural-abundance INEPT ^{15}N NMR spectra on a Bruker WM 400 spectrometer (100.62 and 40.56 MHz, respectively). $^1J_{^{15}N-^1H}$ (73.5 Hz) is the driving coupling in the INEPT experiment.[10] Chemical shifts are given in ppm downfield from internal tetramethylsilane (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P), internal $CFCl_3$ (^{19}F), and external 80/20 (v/v) $MeNO_2$ in C_6D_6 (^{15}N). All experimental procedures were carried out under oxygen-free argon. The solvents were freshly distilled under argon from appropriate drying agents.

Synthesis of $(t\text{-}BuNC)_2(Cl)Rh(\mu\text{-}Cl)Rh(CO)[PhP(OC(CH_3)_2CH_2)_2NH]$ (2). A solution of 26.5 mg (0.32 mmol) of *t*-BuNC in 2 mL of toluene was added to a solution of **1** (100 mg, 0.16 mmol) in 6 mL of toluene with stirring at 0° C. After 1 h, the solution was allowed to warm to room temperature. Evaporation of the solvent led to a pale yellow powder, which was washed with pentane (3 × 10 mL). Recrystallization from a 1/1 mixture of THF/pentane at −30 °C gave 103 mg (0.135 mmol, 85%) of **2** as yellow crystals containing $^1/_3$ mol of THF/mol of **2**, confirmed by ^1H NMR; mp 185 °C. IR (KBr, cm^{-1}): ν(NH) 3260, ν(NC) 2180, ν(CO) 1990, ν(RhCl) 320 and 300. $^{31}P\{^1H\}$ NMR (THF): 147.5 (d, $^1J_{P-Rh}$ = 178.6 Hz). ^1H NMR ($CDCl_3$): 1.39, 2.16 (s, s; 6 H, 6 H; CH_3 exo and endo), 1.45, 1.47 (d, d; $J_{Rh-H} \approx 2$ Hz; 9 H, 9 H; *t*-Bu), 2.76, 2.79, 3.33, 3.41 (d, d, d, d; 1 H, 1 H, 1 H, 1 H; $^2J_{CH-H}$ = 14 Hz; CH exo and endo). ^{13}C NMR (CD_2Cl_2): 190.1 (dd, $^1J_{Rh-C}$ = 93 Hz, $^2J_{P-C}$ = 16 Hz, CO), 182.6 (d, $^1J_{Rh-C}$ = 70 Hz, C═N), 135.5 (d, $^1J_{P-C}$ = 92 Hz, P–C(Ph)), 132.2 (s, *p*-C(Ph)), 130.0 and 128.8 (d, d; J_{P-C} = 15 Hz, J_{P-C} = 13 Hz; *o*- and *m*-C(Ph)), 81.5 (s, O–C), 61.8 (d, J_{P-C} = 8 Hz, N–CH_2), 58.4 (s, ═N–C), 31.7 and 31.0 (s, d; J_{P-C} = 6 Hz; O-C(CH_3)$_2$), 30.4 (s, N–C(CH_3)$_3$). INEPT ^{15}N NMR (CD_2Cl_2): −370 (ddd, $^1J_{N-H}$ = 73.5 Hz, $^1J_{N-Rh} \approx {}^2J_{N-P}$ = 11.8 Hz). Anal. Calcd for $C_{25}H_{40}Cl_2N_3O_3PRh_2\cdot{}^1/_3THF$ (M_r = 762.0): C, 41.46; H, 5.60; N, 5.41. Found: C, 41.39; H, 5.55; N, 5.41.

Synthesis of $(CO)(Cl)Rh(\mu\text{-}Cl)(\mu\text{-}R'C{\equiv}CR')(\mu\text{-}CO)Rh[PhP(OC(CH_3)_2CH_2)_2NH]$. R′ = CO_2Me (DMA), 3a. A solution of DMA (1 mL) in toluene (0.036 M) was added, at room temperature with stirring, to a solution of **1** (23 mg, 0.036 mmol) in 3 mL of toluene. After 3 h, the yellow precipitate was filtered, washed with pentane, and dried under vacuum, leading to 2k mg (0.032 mmol, 89%) of **3a**. **3a** is insoluble in toluene, THF, $CHCl_3$, CH_2Cl_2, and ether and sparingly soluble in CH_3CN, DMF, and Me_2SO, in which it decomposes. IR (KBr, cm^{-1}): ν(NH) 3220, ν(C≡O) 2085 and 1785, ν(C═O) 1695, ν(C≡C) 1555, ν(Rh–Cl) 300 and 290. Anal. Calcd for $C_{22}H_{28}Cl_2NO_8PRh_2\cdot{}^1/_3C_6H_5CH_3$ (M_r = 772.67): C, 37.79; H, 3.97; N, 1.81; P, 4.01. Found: C, 37.64; H, 3.96; N, 1.80; P, 3.85.

R′ = CO_2-*n*-Bu (DBA), 3b. Similarly, **3b** was obtained in 88% yield as a yellow powder, soluble in CH_2Cl_2 and $CHCl_3$ and sparingly soluble in toluene and THF. IR (KBr, cm^{-1}): ν(NH) 3220, ν(C≡O) 2085 and 1785, ν(C═O) 1695, ν(C≡C) 1555, ν(Rh–Cl) 300 and 290. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 147.2 (dd, $^1J_{P-Rh}$ = 229 Hz, $^xJ_{P-Rh}$ = 9 Hz). ^1H NMR ($CDCl_3$): 0.90–1.50 (m, CH_2CH_3 and O–C(CH_3)$_2$), 2.90–4.3 (m, NCH_2 and OCH_2), 6.50 (m, NH), 7.5 (m, C_6H_5). Anal. Calcd for $C_{28}H_{40}Cl_2NO_8PRh_2$ (M_r = 826.4): C, 40.66; H, 4.84; N, 1.69, P, 3.75. Found: C, 40.73; H, 4.80; N, 1.62; P, 3.72.

R′ = CF_3 (HFB), 3c. Gaseous HFB was bubbled for $^1/_2$ h through a magnetically stirred solution of **1** (80 mg, 0.127 mmol) in 10 mL of THF. Evaporating the solvent, washing with pentane, and drying under vacuum led to **3c** as a yellow powder (83 mg, 0.109 mmol, 86%), sparingly soluble in CH_2Cl_2 and $CHCl_3$. IR (KBr, cm^{-1}): ν(NH) 3220, ν(C≡O) 2100 and 1790, ν(C≡C) 1575, ν(Rh–Cl) 310 and 300. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): 145 (dm, $^1J_{P-Rh}$ = 220 Hz). ^{19}F NMR ($CDCl_3$): −50.6 (m, 3 F), −53.0 (dq, $^5J_{F-F}$ = 12 Hz, $^3J_{F-Rh}$ = 3 Hz, 3 F). Anal. Calcd for $C_{20}H_{22}Cl_2F_6NO_4PRh_2\cdot 0.6THF$ (M_r = 762): C, 33.38; H, 3.33; F, 14.16; N, 1.74; P, 3.85. Found: C, 33.39; H, 3.43; F, 14.80; N, 1.69; P, 3.86. The presence of THF is further confirmed by ^1H NMR.

Results and Discussion

Action of *tert*-Butyl Isocyanide. Allowing 1 equiv of *t*-BuNC to react with **1** in toluene at room temperature leads to the substitution not of one but of two carbonyl groups, which results in a mixture of **2** and unreacted **1** in a 1/1 ratio. Under these conditions, a ν(C≡N) stretch at 2190 cm^{-1} and a new ν(C≡O)

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