parison to an authentic sample.

(b) Compound 3 (0.010 g, 0.016 mmol), $AgOSO_2CF_3$ (0.004 g, 0.016 mmol), and benzene-d_6 (0.4 mL) were combined in an NMR tube. As determined by ^1H NMR, immediate reaction occurred with precipitation of Ag^0 to afford 9 and other Si-H compounds (see Results and Discussion).

$Mes_2SiH(OSO_2CF_3)$. Toluene (15 mL) was added to a solid mixture of Mes_2SiHCl (0.975 g, 3.22 mmol) and $AgOSO_2CF_3$ (0.834 g, 3.24 mmol) in an Al-foil-covered flask at -78 °C. The resulting white heterogeneous mixture was warmed to ambient temperature and stirred for 1 h. The volatiles were removed in vacuo, and the pink solid was extracted three times with diethyl ether and filtered. Concentration of the colorless filtrate to 10 mL followed by cooling to -78 °C and filtration gave 0.953 g (71%) of $Mes_2SiH(OSO_2CF_3)$ as an off-white powder. Recrystallization from diethyl ether afforded white crystals (mp 122-124 °C). Mass spectrum: exact mass calcd for $C_{19}H_{23}F_3O_3SSi$, 416.1089; found, 416.1093. IR (Nujol, CsI, cm^{-1}): 3030, 2239 (Si-H), 1607, 1547, 1263 sh, 1248, 1209 s, 1155 s, 1083, 1070 sh, 1035, 958 s, 924, 850 s, 772, 717, 683, 639, 624, 604 sh, 562 sh, 547, 509, 432, 410, 387. ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 1.98 (s, 6 H, p-$C_6H_2(CH_3)_3)_2$, 2.32 (s, 12 H, o-$C_6H_2(CH_3)_3$), 6.32 (s, 1 H, SiH), 6.56 (s, 4 H), $C_6H_2(CH_3)_3$).

$Mes_2SiH(Me)$. MeLi (2.4 mL of a 1.4 M solution in diethyl ether, 3.36 mmol) was added to a solution of Mes_2SiHCl (1.04 g, 3.43 mmol) in tetrahydrofuran (10 mL). After the solution was stirred for 1 h at room temperature, volatiles were removed by vacuum transfer, leaving a white solid. The product was extracted into pentane (15 mL) and crystallized from that solvent at -78 °C. Yield of $Mes_2SiH(Me)$ was 0.658 g (68%). ^1H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.61 (d, 3 H, $SiCH_3$), 2.08 (s, 6 H, p-$C_6H_2(CH_3)_3$), 2.34 (s, 12 H, o-$C_6H_2(CH_3)_3$), 5.50 (q, 1 H, SiH), 6.70 (s, 4 H, $C_6H_2(CH_3)_3$).

$Cp*_2ZrCH_2CCHCMeCHCMeCSiHMes$ (10). (a) A solution of $Cp*ZrCl_2$ (0.375 g, 0.87 mmol) and 1 (0.875 g, 2.1 mmol) in toluene (20 mL) was stirred at ambient temperature for 5 h. Volatiles were removed, and the orange residue was taken up in warm toluene (30 mL, ca. 50 °C) and filtered. Toluene was removed, the resulting deep orange solid was slurried in 10 mL of diethyl ether, and the mixture was filtered. The isolated product was washed thoroughly with diethyl ether and dried in vacuo (mp 234-236 °C). By ^1H NMR the purity of 10 was >95%. Yield of 10: 0.391 g, 72%. Anal. Calcd for $C_{38}H_{52}ZrSi$: C, 72.66; H, 8.34. Found: C, 72.28; H, 8.29. IR (Nujol, CsI, cm^{-1}): 2060 s (Si-H), 1583, 1018, 878, 845, 751, 720, 698.

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Registry No. 1, 117940-80-4; 2, 117940-81-5; 3, 117940-82-6; 4, 117940-83-7; 5, 117940-84-8; 6, 117940-85-9; 7, 117940-86-0; 8, 117940-87-1; 9, 111287-33-3; 10, 117940-88-2; Mes_2SiHCl, 50490-74-9; $Cp_2Zr(Me)Cl$, 1291-45-8; $Cp*_2Zr(Me)Br$, 84987-21-3; $Cp*_2Zr(Me)H$, 117940-89-3; $Cp*_2ZrH_2$, 61396-34-7; $Cp*_2ZrMe_2$, 67108-80-9; $AgOSO_2CF_3$, 2923-28-6; $Mes_2SiH(OSo_2CF_3)$, 117940-79-1; $Mes_2SiH(Me)$, 50490-58-9; $Cp*_2ZrCl_2$, 54039-38-2.

Synthesis and Reactivity toward Nucleophiles of Bis(isocyanide)(porphyrinato)rhodium(III) Complexes. Crystal and Molecular Structure of a Novel Carbene Complex: $\{(TPP)Rh(PhCH_2NC)[:C(NHCH_2Ph)_2]PF_6\}$

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Bis(isocyanide)(octaethylporphyrinato)- and bis(isocyanide)(tetraphenylporphyrinato)rhodium(III) hexafluorophosphates undergo nucleophilic attack leading to the formation of cationic carbene derivatives or neutral carboxymethyl, amido, and alkyl complexes. The formation of the various products is related to the strength of the nucleophile. The crystal and molecular structure of the title compound has been determined by X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions a = 16.427 (7) Å, b = 14.386 (7) Å, c = 13.268 (5) Å, α = 107.83 (4)°, β = 99.51 (4)°, γ = 77.31 (3)°, and Z = 2. The structure was solved by the heavy-atom technique and refined to R = 0.0773 for 3991 independent reflections. The rhodium atom is at the center of a slightly distorted octahedral environment.

Introduction

Rhodium porphyrinates have been the subject of many studies because of the versatile redox behavior of the central metal atom and their possible applications as photocatalysts and as models for biological systems.[1-6] During our studies of the influence of monodentate axial ligands on the redox behavior and reactivity of metalloporphyrinates, we have synthesized and characterized some hexacoordinated rhodium(III) derivatives of octaethyl- (OEP) and *meso*-tetraphenylporphyrin (TPP).[7,8] These

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(1) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 142.

(2) Kadish, K. M.; Yao, C. L.; Anderson, J. E.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 4515.

(3) Lever, A. B. P.; Ramaswamy, B. S.; Licoccia, S. *J. Photochem.* **1982**, *19*, 173.

(4) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

(5) Aoyama, Y.; Watanabe, T.; Onda, H.; Ogoshi, H. *Tetrahedron Lett.* **1983**, *24*, 1183.

(6) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983.

0276-7333/89/2308-0330$01.50/0

ligands have been chosen because the TPP and OEP dianions are respectively among the weakest and strongest porphyrin donors and represent two extremes in the electronic properties of such macrocycles.[6] There is in fact an inversion in the energy of the two HOMO's (a_{1u} and a_{2u}) in their π systems.[9]

Since the catalytic role of metalloporphyrins is certainly dependent on the chemistry of axial ligands,[10] we decided to investigate the reactions between bis(isocyanide) derivatives and nucleophiles. It is well-known that isocyanides coordinated to transition metals react with alcohols or amines leading to the formation of carbene compounds and, although many papers have dealt with palladium and platinum complexes, very little has been published on rhodium derivatives.[11-14] As far as carbene complexes of tetrapyrrole macrocycles are concerned, Mansuy[15] reported on the synthesis of some iron porphyrin complexes with $:CX_2$ ligands. The possibility of modifying the *p*-tolyl isocyanide ligand in a cobalt(III) corrole derivative has also been investigated,[16] but this compound proved to be stable in refluxing methanol, and no modification or dissociation of the axial ligand was observed. Other authors[17] have postulated the formation of RhTPP–carbene intermediates in the catalytic cyclopropanation of *cis*-olefins but did not even attempt to isolate such compounds.

We now report the synthesis of rhodium porphyrin carbene complexes which are, to our knowledge, the first examples of fully characterized carbene complexes of a rhodium macrocycle.

Experimental Section

IR spectra were recorded on a Perkin Elmer Model 983 spectrophotometer as Nujol mulls. NMR spectra were recorded on a Bruker WP 80 SY instrument as C^2HCl_3 solutions with tetramethylsilane (TMS) as the internal standard.

All solvents were reagent grade and were used without further purification.

[(TPP)RhCl] and [(OEP)Rh(DMA)$_2$Cl] have been prepared according to literature procedures.[7-18] [PRh(CNR)$_2$PF$_6$] (P = OEP, TPP; R = CH$_2$Ph, *p*-ClPh) have been synthesized following the procedure previously reported.[8]

Reactions of [PRh(CNR)$_2$PF$_6$] with Nucleophiles (P = OEP, TPP; R = *t*-BuNC, *p*-ClPh, CH$_2$Ph). (a) Reactions with Methanol. [PRh(CNR)$_2$PF$_6$] complexes (2 × 10^{-4}mol) were refluxed in methanol (100 mL). The reaction time was 32 h for the *p*-chlorophenyl and 72 h for the benzyl derivative, respectively. When R = *t*-Bu, even after a short time (less than 12 h), a product is obtained, the nature of which was not investigated because it was insoluble in most organic solvents. The only solid-state measurement we performed (IR spectrum) showed that it still contained a coordinated isocyanide.

For the *p*-chlorophenyl and benzyl derivatives, the reaction solution was vacuum evaporated and the residue column chromatographed on silica gel (eluant chloroform). Two bands were separated: recrystallization from methanol of the first one afforded orange crystals of [PRh(CO$_2$CH$_3$)] (yield 2 × 10^{-5} mol (10%)), while the second one, recrystallized from chloroform/*n*-hexane (1:2), yielded purple crystals of {PRh:C(NHR)$_2$PF$_6$} (yield 1 × 10^{-4} mol (50%)).

(b) Reactions with Methoxide. The starting compounds (2 × 10^{-4} mol) were added to a freshly prepared solution of methoxide in methanol (100 mL) and refluxed for 3 h. The solvent was evaporated under reduced pressure and the residue worked up as in (a). Pure crystals of [PRhCH$_3$][19-21] were obtained by recrystallization from methanol (yield 1.6 × 10^{-4} mol (80%)).

(c) Reactions with Phenoxide. PhO$^-$ was prepared by the addition of Na to a solution of PhOH in THF. [PRh(CNR)$_2$PF$_6$] complexes (2 × 10^{-4} mol) were added, and the mixture was kept refluxing for 3 h. The crude materials were worked up as in (a). Recrystallization from methanol afforded the amido complexes [PRh(CONHR)] (yield 1 × 10^{-4} mol (50%)). When P = TPP and R = CH$_2$Ph, the reaction product was [(TPP)Rh(CH$_2$Ph)].

Synthesis of [PRhLL′PF$_6$] Complexes [P = TPP, L = :C(NHCH$_2$Ph)$_2$, L′ = PPh$_3$, P(OMe)$_3$, PhCH$_2$NC; P = OEP, L = :C(NHCH$_2$Ph)$_2$, L′ = P(OMe)$_3$]. The parent compound {PRh[:C(NHCH$_2$Ph)$_2$]PF$_6$} (2 × 10^{-4} mol) was dissolved in chloroform (100 mL), and excess L′ was added. The solution was kept stirring at room temperature for 2 h. Pure products were obtained by column chromatography on silica gel (eluant chloroform) and recrystallization from chloroform/*n*-hexane (1:2). Yields were always higher than 80%.

X-ray Crystallography. Data Collection and Reduction. Red prismatic crystals of the title compound suitable for X-ray diffraction studies were obtained by recrystallization from a methylene chloride–hexane mixture, but, due to difficulties encountered in growing crystals, it was not possible to select a specimen for data collection having dimensions greater than 0.07 × 0.08 × 0.52 mm.

All diffraction work was carried out on a Siemens AED single-crystal computer-controlled diffractometer. A reciprocal lattice search revealed no systematic extinctions or symmetry, indicating a triclinic lattice which was confirmed by reduced cell calculations. The ambiguity in the space group $P1$ or $P\bar{1}$ was solved by analysis of intensity distribution statistics, which gave a clear indication of centricity. The structure was thus solved in the centrosymmetric space group $P\bar{1}$, which proved later to be the correct one. The unit-cell parameters and their estimated standard deviations were determined by least-squares fit of diffractometer measured 2θ values for 30 reflections chosen in different regions of reciprocal space. Crystal data are as follows: $C_{67}H_{51}F_6N_7PRh$, M = 1202.06, a = 16.427 (7) Å, b = 14.386 (7) Å, c = 13.268 (5) Å, α = 107.83 (4)°, β = 99.51 (4)°, γ = 77.31 (3)°, V = 2896 (2) Å^3, Z = 2, D_{calcd} = 1.379 g cm^{-3}; Cu Kα radiation (λ = 1.54178 Å); μ(Cu Kα) = 32.46 cm^{-1}.

The intensities were measured at room temperature with Cu Kα radiation[22] using a θ–2θ step–scanning technique with a scan speed ranging from 3 to 12°/min. One hemisphere of data ($\pm h$, $\pm k$, $+l$) was collected within the 2θ limits of 6.0–110.0°, and in this way a total of 6920 reflections was examined, 3991 of which, having $I > 2\sigma(I)$, were retained as observed for structural refinement. The intensity of a standard reflection, checked after every 50 measurements to assess possible crystal movement or deterioration, showed only small random fluctuations. Peak profile analysis was performed with a local modification of the Lehmann

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(7) Boschi, T.; Licoccia, S.; Tagliatesta, P. *Inorg. Chim. Acta* **1986**, *119*, 191.

(8) Boschi, T.; Licoccia, S.; Tagliatesta, P. *Inorg. Chim. Acta* **1987**, *126*, 157.

(9) Dolphin, D.; Muljiani, Z.; Roussear, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 177.

(10) (a) Hambright, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1976. (b) La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D. H., Ed., Academic Press: New York, 1979; Vol. IV.

(11) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545.

(12) Bonati, F.; Minghetti, G., Boschi, T.; Crociani, B. *J. Organomet. Chem.* **1970**, *25*, 255.

(13) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021.

(14) Mague, J. T. *J. Organomet. Chem.* **1986**, *305*, 34.

(15) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681.

(16) Conlon, M.; Johnson, A. W.; Overend, W. R.; Rajapaksa, D.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2281.

(17) Callot, J. H.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489.

(18) Fleisher, E. B.; Thorp, R.; Venrable, D. *J. Chem. Soc., Chem. Commun.* **1969**, 465.

(19) Ogoshi, H.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1973**, *95*, 1666.

(20) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461.

(21) Anderson, J. E.; Yao, C. L.; Kadish, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 1106.

(22) The choice of the radiation used to collect intensity data is worthy of some comment. Initially an attempt to collect the data set with the same crystal by using Mo Kα radiation (more suitable to be used for a sample of such a chemical composition) was made, but the diffraction maxima located in the search routine were so low in intensity to discourage us from undertaking data collection.

Table I. Fractional Atomic Coordinates (×10^5 for Rh and ×10^4 for Other Atoms)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Rh	18309 (5)	19287 (6)	39529 (7)	C(36)	−2271 (4)	1827 (6)	128 (6)
N(1)	2114 (5)	2016 (7)	5545 (8)	C(37)	−1789 (4)	947 (6)	293 (6)
N(2)	3054 (6)	1856 (6)	3847 (8)	C(38)	−1034 (4)	968 (6)	953 (6)
N(3)	1549 (6)	1845 (7)	2364 (8)	C(39)	247 (4)	1816 (5)	6759 (5)
N(4)	597 (5)	2015 (6)	4040 (7)	C(40)	172 (4)	845 (5)	6668 (5)
N(5)	2211 (6)	−379 (8)	3790 (8)	C(41)	−257 (4)	658 (5)	7389 (5)
N(6)	2245 (6)	3911 (6)	4870 (8)	C(42)	−611 (4)	1442 (5)	8201 (5)
N(7)	977 (6)	3885 (7)	3766 (9)	C(43)	−536 (4)	2413 (5)	8292 (5)
C(1)	1567 (8)	1997 (7)	6212 (11)	C(44)	−107 (4)	2600 (5)	7571 (5)
C(2)	1997 (8)	1973 (8)	7220 (10)	C(45)	2063 (7)	415 (10)	3743 (10)
C(3)	2810 (8)	1971 (9)	7162 (12)	C(46)	2382 (8)	−1419 (9)	3881 (11)
C(4)	2886 (7)	1986 (8)	6092 (10)	C(47)	2707 (6)	−1418 (7)	5011 (7)
C(5)	3638 (7)	1904 (9)	5685 (10)	C(48)	2505 (6)	−616 (7)	5894 (7)
C(6)	3716 (8)	1864 (9)	4615 (11)	C(49)	2786 (6)	−702 (7)	6919 (7)
C(7)	4468 (8)	1812 (11)	4201 (13)	C(50)	3269 (6)	−1588 (7)	7060 (7)
C(8)	4284 (8)	1779 (10)	3172 (13)	C(51)	3472 (6)	−2390 (7)	6177 (7)
C(9)	3403 (7)	1814 (8)	2917 (10)	C(52)	3191 (6)	−2304 (7)	5152 (7)
C(10)	2967 (8)	1761 (8)	1918 (10)	C(53)	1664 7)	3423 (7)	4230 (9)
C(11)	2108 (8)	1794 (8)	1668 (10)	C(54)	2311 (8)	4990 (8)	5204 (11)
C(12)	1651 (9)	1759 (9)	630 (10)	C(55)	3117 (4)	5082 (6)	5929 (7)
C(13)	842 (9)	1797 (9)	726 (11)	C(56)	3076 (4)	5571 (6)	7009 (7)
C(14)	759 (7)	1829 (8)	1777 (10)	C(57)	3812 (4)	5708 (6)	7687 (7)
C(15)	18 (6)	1911 (7)	2203 (10)	C(58)	4589 (4)	5356 (6)	7285 (7)
C(16)	−49 (7)	1999 (7)	3262 (10)	C(59)	4630 (4)	4867 (6)	6205 (7)
C(17)	−821 (8)	2089 (9)	3701 (12)	C(60)	3894 (4)	4730 (6)	5527 (7)
C(18)	−635 (7)	2098 (9)	4722 (12)	C(61)	756 (9)	4918 (9)	3678 (12)
C(19)	262 (7)	2037 (8)	4976 (10)	C(62)	29 (4)	4970 (6)	2829 (7)
C(20)	700 (7)	1974 (7)	5972 (9)	C(63)	156 (4)	4634 (6)	1754 (7)
C(21)	4425 (5)	1842 (7)	6430 (7)	C(64)	−515 (4)	4754 (6)	981 (7)
C(22)	4696 (5)	2704 (7)	7084 (7)	C(65)	−1314 (4)	5208 (6)	1285 (7)
C(23)	5460 (5)	2641 (7)	7721 (7)	C(66)	−1441 (4)	5543 (6)	2361 (7)
C(24)	5954 (5)	1715 (7)	7703 (7)	C(67)	−770 (4)	5424 (6)	3133 (7)
C(25)	5684 (5)	852 (7)	7049 (7)	P	7345 (2)	4453 (3)	7845 (4)
C(26)	4919 (5)	916 (7)	6412 (7)	F(1)	6731 (7)	5072 (7)	8698 (8)
C(27)	3468 (6)	1668 (7)	1026 (7)	F(2)	7927 (6)	3819 (6)	6928 (7)
C(28)	3715 (6)	2510 (7)	950 (7)	F(3)	7338 (9)	3426 (11)	8063 (12)
C(29)	4182 (6)	2437 (7)	133 (7)	F(4)	8160 (8)	4586 (9)	8645 (10)
C(30)	4403 (6)	1523 (7)	−609 (7)	F(5)	7394 (10)	5404 (10)	7480 (13)
C(31)	4156 (6)	680 (7)	−533 (7)	F(6)	6577 (11)	4273 (14)	6953 (14)
C(32)	3689 (6)	753 (7)	284 (7)	F(3′)	7483 (28)	3697 (32)	8602 (37)
C(33)	−761 (4)	1869 (6)	1447 (6)	F(4′)	7826 (32)	5368 (36)	8400 (41)
C(34)	−1243 (4)	2747 (6)	1282 (6)	F(5′)	6848 (22)	5127 (24)	7116 (25)
C(35)	−1998 (4)	2727 (6)	622 (6)	F(6′)	6597 (20)	3814 (24)	7315 (27)

and Larsen procedure,[23] and the intensity data were corrected for Lorentz and polarization factors. Corrections for absorption and extinction effects were applied during the refinement according to the empirical method of Walker and Stuart.[24]

Structure Determination and Refinement. The structure was solved by conventional heavy-atom technique.[5] The position of the rhodium atom was determined by interpretation of a three-dimensional Patterson map. After initial refinement of the metal atom coordinates, the remaining non-hydrogen atoms were located from subsequent Fourier and difference Fourier syntheses. In order to have a better observations/parameters ratio all the seven phenyl rings were treated as rigid groups of D_{6h} symmetry. For the same reason the carbon atoms of four of these rings, namely, those of the TPP moiety, as well as the fluorine atoms, were assigned isotropic thermal parameters, while the remaining non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms attached to the pyrrole ring carbons were located from a difference Fourier map and included in the last refinement cycle together with the hydrogen atoms bonded to the phenyl ring carbons, which were incorporated at calculated "riding" positions. Other hydrogens could not be located. The PF_6^- anion showed orientational disorder about a common phosphorus site with two of the six fluorine atoms occupying the same position in both orientations. It was refined as two components with an occupancy ratio of 0.75/0.25. The quantity minimized was $\sum w|\Delta F^2|$, where w is the weight of a given observation. Initially unit weights were used, while during the final stages of refinement a weighting scheme of the type $0.3151/\sigma^2(F_o) + 0.02206F_o^2$ was applied. The final model converged to $R = 0.0773$ for 554 variables refined. The not completely satisfactory value of R is an unavoidable consequence of the dominating role of Rh in the scattering power of a crystal of such a small size. In the final difference map the top for residual peaks had heights of 1.37–0.96 e Å^{-3} and were 1.2–1.3 Å from the metal atom.

The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of the anomalous dispersion.[25] The major calculations were carried out with the program package SHELX-76[26] on a GOULD-SEL 32/77 computer. The other programs used in the structure determination have been cited elsewhere.[27]

Atomic coordinates for non-hydrogen atoms are given in Table I and selected bond distances and angles in Table II.

Observed and calculated structure factors, H-atom coordinates, thermal parameters, and all bond distances and angles are available as supplementary material.

Results and Discussion

Rhodium(III) porphyrin complexes easily react with isocyanides, in the presence of silver hexafluorophosphate, leading to the formation of $[PRh(CNR)_2PF_6]$ (P = OEP, TPP; R = CH_2Ph, *p*-ClPh) complexes following the pro-

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[23] Lehman, M. S.; Larsen, F. K. *Acta Crystallogr.* **1983**, *A30*, 580.

[24] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[25] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

[26] Sheldrick, G. M. SHELX-76, A program for Crystal Structure Determination; University of Cambridge: Cambridge, U.K., 1976.

[27] Delledonne, D.; Pelizzi, G.; Pelizzi, C. *Acta Crystallogr.* **1987**, *C43*, 1502.

Table II. Selected Bond Distances (Å) and Angles (deg)

Rh–N(1)	2.057 (10)	N(1)–C(1)	1.37 (2)	N(3)–C(11)	1.38 (2)
Rh–N(2)	2.015 (10)	C(1)–C(2)	1.41 (2)	C(11)–C(12)	1.45 (2)
Rh–N(3)	2.054 (11)	C(2)–C(3)	1.35 (2)	C(12)–C(13)	1.34 (2)
Rh–N(4)	2.024 (9)	C(3)–C(4)	1.45 (2)	C(13)–C(14)	1.41 (2)
Rh–C(45)	2.064 (13)	C(4)–N(1)	1.35 (1)	C(14)–N(3)	1.40 (1)
Rh–C(53)	2.030 (11)	C(4)–C(5)	1.40 (2)	C(14)–C(15)	1.39 (2)
C(45)–N(5)	1.13 (2)	C(5)–C(6)	1.43 (2)	C(15)–C(16)	1.39 (2)
N(5)–C(46)	1.50 (2)	N(2)–C(6)	1.36 (2)	N(4)–C(16)	1.35 (1)
C(46)–C(47)	1.51 (2)	C(6)–C(7)	1.41 (2)	C(16)–C(17)	1.44 (2)
C(53)–N(6)	1.34 (1)	C(7)–C(8)	1.34 (2)	C(17)–C(18)	1.34 (2)
N(6)–C(54)	1.50 (2)	C(8)–C(9)	1.42 (2)	C(13)–C(19)	1.44 (2)
C(54)–C(55)	1.51 (1)	C(9)–N(2)	1.42 (2)	C(19)–N(4)	1.43 (2)
C(53)–N(7)	1.34 (1)	C(9)–C(10)	1.39 (2)	C(19)–C(20)	1.41 (2)
N(7)–C(61)	1.49 (2)	C(10)–C(11)	1.39 (2)	C(20)–C(1)	1.41 (2)
C(61)–C(62)	1.51 (2)				
N(1)–Rh–N(2)	89.3 (4)	Rh–N(1)–C(4)	126.4 (8)	Rh–N(4)–C(19)	123.9 (8)
N(1)–Rh–N(3)	179.8 (4)	N(1)–C(4)–C(5)	126.4 (11)	N(4)–C(19)–C(20)	128.2 (11)
N(1)–Rh–N(4)	91.6 (4)	C(4)–C(5)–C(6)	125.3 (11)	C(19)–C(20)–C(11)	122.2 (11)
N(1)–Rh–C(45)	84.5 (5)	C(5)–C(6)–N(2)	123.1 (12)	C(20)–C(1)–N(1)	127.6 (12)
N(1)–Rh–C(53)	92.8 (4)	C(6)–N(2)–Rh	129.4 (8)	C(1)–N(1)–Rh	125.8 (8)
N(2)–Rh–N(3)	90.7 (4)	Rh–N(2)–C(9)	125.6 (8)	Rh–C(45)–N(5)	169.6 (11)
N(2)–Rh–N(4)	179.0 (4)	N(2)–C(9)–C(10)	125.8 (12)	C(45)–N(6)–C(46)	177.9 (12)
N(2)–Rh–C(45)	89.1 (5)	C(9)–C(10)–C(11)	125.9 (12)	N(5)–C(46)–C(47)	109.6 (10)
N(2)–Rh–C(53)	88.6 (4)	C(10)–C(11)–N(3)	125.6 (12)	Rh–C(53)–N(6)	118.9 (8)
N(3)–Rh–N(4)	88.5 (4)	C(11)–N(3)–Rh	126.3 (9)	C(53)–N(6)–C(54)	131.4 (10)
N(3)–Rh–C(45)	95.7 (5)	Rh–N(3)–C(14)	127.0 (8)	N(6)–C(54)–C(55)	106.4 (9)
N(3)–Rh–C(53)	87.0 (4)	N(3)–C(14)–C(15)	124.5 (11)	Rh–C(53)–N(7)	118.9 (8)
N(4)–Rh–C(45)	91.5 (5)	C(14)–C(15)–C(16)	125.6 (11)	C(53)–N(7)–C(61)	130.6 (11)
N(4)–Rh–C(53)	90.8 (4)	C(15)–C(16)–N(4)	125.3 (11)	N(7)–C(61)–C(62)	108.3 (10)
C(45)–Rh–C(53)	176.5 (5)	C(16)–N(4)–Rh	129.1 (8)	N(6)–C(53)–N(7)	122.2 (11)

Table III. Spectral Properties for [PRh(CNR)$_2$PF$_6$] Complexes

P	R	IR $\nu_{C\equiv N}$ (cm^{-1})	^{1}H NMR (ppm)
TPP	Bz	2248	9.05 (s, 8H) 8.13–7.75 (m, 20 H) 7.06–6.80 (m, 6 H) 4.91 (d, 4 H) 2.42 (s, 4 H)
OEP	Bz	2238	10.32 (s, 4 H) 6.86–6.77 (m, 6 H) 4.67 (d, 4 H) 4.21 (q, 16 H) 2.02 (t, 24 H)
TPP	*p*-ClPh	2203	9.16 (s, 8 H) 8.37–7.62 (m, 20 H) 6.16 (d, 4 H) 4.16 (d, 4 H)
OEP	*p*-ClPh	2197	10.40 (s, 4 H) 6.04 (d, 4 H) 4.22 (q, 16 H) 3.87 (d, 4 H) 1.97 (t, 24 H)

cedure previously reported for the synthesis of *bis(tert*-butyl isocyanide)(porphyrinato)rhodium(III) hexafluorophosphate.[8]

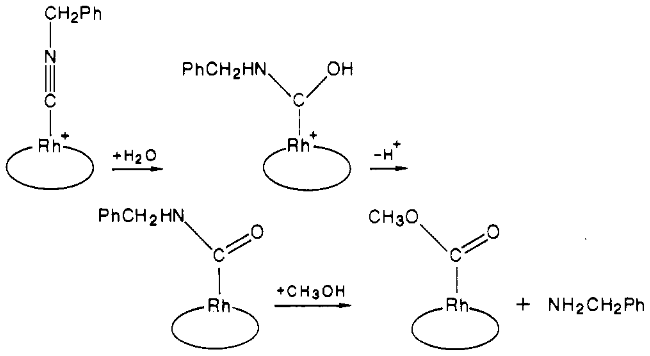
In the IR spectra of the newly synthesized complexes (Table III), the asymmetric N≡C stretching modes appear as strong absorptions in the range 2200–2250 cm^{-1}. The shift to higher frequency after coordination ($74 < \Delta\nu < 98$ cm^{-1}) is related to the main σ character of the metal–isocyanide bond[3] and suggests that the coordinated ligand can undergo nucleophilic attack.

Bis(isocyanide)(porphyrinato)rhodium(III) hexafluorophosphate complexes have then been reacted with weak nucleophiles such as methanol. The main products of these reactions are carbene complexes formulated as {PRh[:C(NHR)$_2$]PF$_6$}. Elemental analyses and spectral properties are reported in Tables IV and V.

In the IR spectra of carbene complexes, the sharp NH stretching bands fall in the range 3250–3380 cm^{-1}. The presence of the hexafluorophosphate counterion is confirmed by a strong absorption at 840 cm^{-1}.[28]

As far as the axial ligands resonances are concerned, the ^{1}H NMR spectra show a strong upfield shift, which can be explained in terms of anisotropic effects due to the macrocycle ring current.[29,30] The nitrogen-bound protons give rise to broad multiplets around −2.00 ppm. In the case of the benzyl derivative, this proton was coupled to the benzyl methylene group (*J* = 5 Hz), as shown by double-resonance experiments.

[PRh(CO$_2$CH$_3$)] complexes have been isolated as secondary products of the reactions with methanol together with traces of [PRh(CONHR)]. The carbonyl stretching (1690 cm^{-1} when P = OEP and 1696 cm^{-1} when P = TPP) is almost coincident with that reported for [(TPP)Rh(CO$_2$C$_2$H$_5$)].[31] This observation and the diagnostic methyl resonances (0.78 and 0.97 ppm, respectively, for OEP and TPP) together with analytical data and mass spectra allowed a straightforward identification of the methoxycarbonyl derivatives (Tables VII and VIII). The formation of such complexes may be explained through the following scheme:



Nucleophilic attack of the amine formed on a coordinated

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(28) Nakamoto, K. In *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1970.

(29) Inhofen, H. H.; Furhop, J. H.; Voight, H.; Brockmann, H. *Ann. Chem.* **1966**, *695*, 133.

(30) Storm, C. B. *J. Am. Chem. Soc.* **1979**, *92*, 1424.

(31) Cohen, I. A.; Chow, B. C. *Inorg. Chem.* **1974**, *13*, 488.

Table IV. Elemental Analyses for [PRhLL′PF$_6$] Complexes

			C		H		N	
P	L	L′	calcd	found	calcd	found	calcd	found
TPP	:C(NHBz)$_2$	···	65.30	64.76	4.08	4.38	7.75	7.67
OEP	:C(NHBz)$_2$	···	60.95	60.71	6.01	6.10	8.36	8.42
TPP	:C(NHBz)$_2$	CNBz	66.94	66.45	4.27	3.95	8.15	7.95
TPP	:C(NHBz)$_2$	P(OMe)$_3$	63.21	62.41	4.53	4.44	7.13	7.12
TPP	:C(NHBz)$_2$	PPh$_3$	67.18	67.95	4.62	4.12	6.52	6.31
OEP	:C(NHBz)$_2$	P(OMe)$_3$	53.38	53.28	5.43	6.01	7.18	7.22
TPP	:C(NH-*p*-ClPh)$_2$	···	60.81	60.53	3.40	3.35	7.46	7.40
OEP	:C(NH-*p*-ClPh)$_2$	···	56.27	57.04	5.20	4.94	8.04	8.16
TPP	CNBz	CNBz	65.81	65.10	3.86	4.05	7.67	7.83
OEP	CNBz	CNBz	61.53	61.20	5.76	5.46	8.28	8.18
TPP	CN-*p*-ClPh	CN-*p*-ClPh	61.33	61.54	3.19	3.06	7.40	7.28
OEP	CN-*p*-ClPh	CN-*p*-ClPh	56.88	57.00	4.96	4.85	7.96	7.75

Table V. Spectral Properties for {PRh[:C(NHR)$_2$]PF$_6$} Complexes

P	R	IR ν_{NH} (cm^{-1})	^{1}H NMR (ppm)
TPP	Bz	3388	8.88 (s, 8H) 8.01–7.75 (m, 20 H) 7.10–7.00 (m, 6 H) 5.32 (d, 4 H) 2.02 (d, 4 H) −1.90 (m, br, 2 H)
OEP	Bz	3377	10.23 (s, 4 H) 7.10–6.92 (m, 6 H) 5.15 (d, 4 H) 4.10 (q, 16 H) 1.94 (m, 28 H) −2.75 (m, br, 2 H)
TPP	*p*-ClPh	3254	8.80 (s, 8 H) 8.20–7.80 (m, 20 H) 5.88 (d, 4 H) 2.24 (d, 4 H) −3.02 (m, br, 2 H)
OEP	*p*-ClPh	3253	10.26 (s, 4 H) 5.66 (d, 4 H) 4.17 (q, 16 H) 2.00 (t, 24 H) 1.81 (d, 4 H) −3.90 (m, br, 2 H)

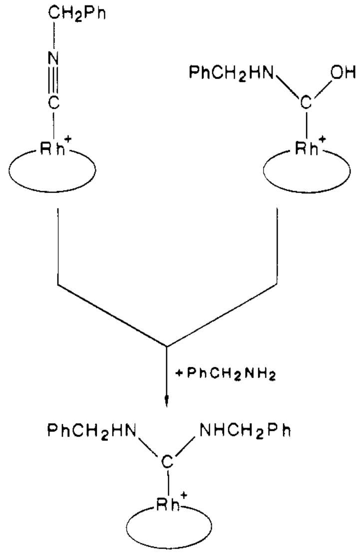
Table VI. Spectral Properties for {PRh[:C(NHBz)$_2$]LPF$_6$} Complexes

		IR (cm^{-1})		
P	L	ν_{NH}	$\nu_{C\equiv N}$	^{1}H NMR (ppm)
TPP	CNBz	3390	2227	8.88 (s, 8 H) 7.99–7.75 (m, 20 H) 7.08–6.81 (m, 9 H) 5.31 (d, 4 H) 4.87 (d, 2 H) 2.48 (s, 2 H) 2.09 (d, 4 H) −1.95 (m, br, 2 H)
TPP	P(OMe)$_3$	3390		8.88 (s, 8 H) 8.10–7.80 (m, 20 H) 7.10–7.01 (m, 6 H) 5.33 (d, 4 H) 2.08 (d, 4 H) 0.78 (d, 9 H, J(P–H) = 10 Hz) −1.75 (m, br, 2 H)
TPP	PPh$_3$	3392		8.78 (s, 8 H) 8.11–7.75 (m, 20 H) 7.05–6.46 (m, 15 H) 5.34 (d, 4 H) 3.93–3.71 (m, 6 H) 1.99 (d, 4 H) −2.36 (m, br, 2 H)
OEP	P(OMe)$_3$	3378		10.15 (s, 4 H) 7.06–6.98 (m, 6 H) 5.09 (d, 4 H) 4.10 (q, 16 H) 1.90 (t, 24 H) 0.42 (d, 9 H, J(P–H) = 10 Hz) −2.50 (m, br, 2 H)

Table VII. Spectral Properties for [PRhL] Complexes

		IR (cm^{-1})		
P	L	ν_{NH}	$\nu_{C=O}$	^{1}H NMR (ppm)
TPP	CONH-*t*-Bu	3417	1696	8.82 (s, 8 H) 8.26–7.69 (m, 20 H) −0.76 (s, 9 H) −2.70 (br, 1 H)
OEP	CONH-*t*-Bu	3420	1680	10.11 (s, 4 H) 4.08 (q, 16 H) 1.94 (t, 24 H) −1.05 (s, 9 H) −3.34 (br, 1 H)
OEP	CONHBz	3419	1664	10.15 (s, 4 H) 6.81–6.73 (m, 3 H) 4.97 (d, 2 H) 4.08 (q, 16 H) 1.93 (t, 24 H) −2.62 (br, 1 H)
TPP	Bz			8.69 (s, 8 H) 8.15–7.80 (m, 20 H) 6.45 (m, 1 H) 5.91 (m, 2 H) 3.06 (m, 2 H) −3.74 (d, 2 H)
TPP	CO$_2$CH$_3$		1696	8.82 (s, 8 H) 8.28–7.72 (m, 20 H) 0.97 (s, 3 H)
OEP	CO$_2$CH$_3$		1690	10.15 (s, 4 H) 4.10 (q, 16 H) 1.93 (t, 24 H) 0.78 (s, 3 H)

isocyanide or on one of the hypothetical intermediates might then generate the carbene complexes:



In order to confirm such a scheme bis(isocyanide)(tetraphenylporphyrinato)rhodium(III) hexafluorophosphate

Table VIII. Elemental Analyses for [PRhL] Complexes

P	L	C calcd	C found	H calcd	H found	N calcd	N found
TPP	CO(NH-*t*-Bu)	72.14	71.67	4.69	4.62	8.58	8.26
OEP	CO(NH-*t*-Bu)	66.92	67.14	7.40	7.23	9.51	9.12
OEP	CO(NHBz)	68.64	68.05	6.81	6.93	9.09	8.70
TPP	CO_2CH_3	71.32	70.88	4.03	3.95	7.23	6.70
OEP	CO_2CH_3	65.69	65.11	6.82	6.22	8.06	7.88
TPP	Bz	74.21	74.65	4.90	4.92	7.36	7.12

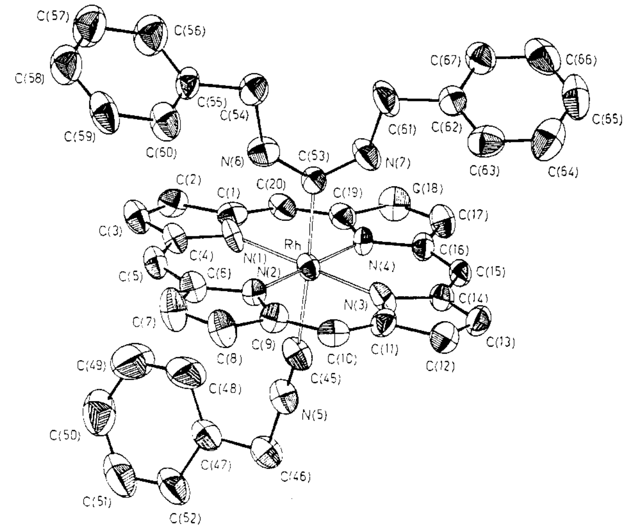


Figure 1. ORTEP diagram of the $[Rh(TPP)(PhCH_2NC)\{:C(NHCH_2Ph)_2\}]^+$ cation. The peripheral phenyl rings have been omitted for clarity, and the thermal ellipsoids have been drawn at the 40% probability level.

has been reacted with benzylamine in THF. The reaction gives a complex mixture of products that could not be separated. However, the resonances typical of the expected carbene complex were present in the NMR spectrum of the crude product.

Since the stretching of the NC bonds in the IR spectrum of $[PRh(t\text{-}BuNC)_2PF_6]$ fall at about 2220 cm^{-1} ($\Delta\nu$ (after coordination) = 90 cm^{-1}), electronic effects cannot explain the lack of formation of the corresponding carbene derivatives which may be attributed only to steric factors.

The present carbene complexes react with ligands (L = $P(OMe)_3$, PPh_3, $PhCH_2NC$) leading to the formation of cationic hexacoordinated species $\{PRhL[C(NHR)_2]PF_6\}$. Their spectral properties are reported in Table VI.

In the NMR spectrum (Figure 1) of the complex $\{(TPP)Rh(BzNC)[:C(NHBz)_2]PF_6\}$, the doublets at 5.31 and 4.87 ppm have been attributed to the resonances of the ortho protons of the carbenic and isocyanide ligands, respectively. The shielding effect of the porphyrin ring is higher in the case of the isocyanide ligand because of its linear geometry. The resonances due to the methylenic groups appear as a poorly resolved doublet centered at 2.09 ppm for the carbene ligand and as a singlet-at 2.48 ppm for the coordinated isocyanide. The apparent inversion in the chemical shift of these two groups is probably due to the shielding effect of the nitrogen carbon triple bond which is opposite to the one of the porphyrin.

In order to elucidate the reaction mechanism, bis(isocyanide) derivatives have been reacted with stronger nucleophiles such as phenoxide and methoxide. The reaction rates and the nature of the products appear to be highly influenced by the strength of the nucleophile. Thus, neutral amido complexes are formed, in about 3 h, when the nucleophile used is phenoxide. The reaction does not proceed toward the carbene derivative probably because

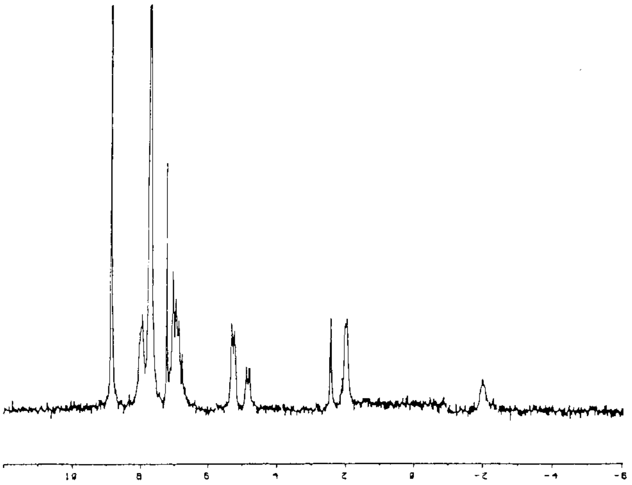


Figure 2. The 80-MHz ^1H NMR spectrum of $\{TPPRh(CNBz)[:C(NHBz)_2]PF_6\}$ in C^2HCl_3 at 308 K.

a further attack of phenoxide on the coordinated amide would generate an highly hindered intermediate. Spectral properties and elemental analyses are reported in Tables VII and VIII.

A different product, $[(TPP)RhCH_2Ph]$, has been isolated from the reaction of $[(TPP)Rh(PhCH_2NC)_2PF_6]$. This complex probably originates from an intramolecular transfer of the benzyl group in the corresponding amido derivative. A similar intramolecular alkyl transfer has been observed[32] in the reaction of (TPP)RhCl with *N*,*N*-diethylformamide.

When methoxide is used, [PRhMe][20,21] complexes have been isolated together with small amounts of amido derivatives. The above complexes are also formed by the reaction of $[PRhCO_2CH_3]$ with methoxide. The reaction probably proceeds through nucleophilic attack performed by methoxide on the methoxycarbonyl derivatives leading to the product with elimination of alkyl carbonates.

These results seem to indicate that all the reactions proceed according to the proposed schemes and that all the complexes synthesized are derived from consecutive reactions occurring on the axial ligands, such as hydrolysis and decarboxylation.

Crystal and Molecular Structure of $\{(TPP)Rh(CNBz)[:C(NHBz)_2]PF_6\}$. The crystal structure consists of discrete $\{Rh(TPP)(PhCH_2NC)[:C(NHCH_2Ph)_2]\}^+$ cations and PF_6^- anions, with no unusually short intermolecular contacts. A perspective view of the cation, along with the atomic numbering scheme, is given in Figure 2 with thermal ellipsoids representing 40% probability boundaries. The coordination sphere of the rhodium atom, which lies at the centroid of the porphyrin moiety, consists of four pyrrole nitrogen atoms, one carbon atom from the carbene ligand, and one carbon atom from the isocyanide group. The geometry of the coordination polyhedron may be described as a slightly distorted octahedron. Bond angles at rhodium show only small deviations from the ideal octahedral values as they are in the range 84.5 (5)–95.7 (5)° (cis angles) and 176.5 (5)–179.8 (4)° (trans angles). The most significant deviation among these angles involves the isocyanide carbon atom. The Rh–N bond distances are all nearly equivalent, lying in the narrow range 2.015 (10)–2.057 (10) Å, even though a closer examination shows that the two adjacent Rh–N bonds differ slightly from each other, in agreement with earlier findings.[33] The average

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[32] Boschi, T.; Licoccia, S.; Tagliatesta, P. *Inorg. Chim. Acta* **1988**, *143*, 235.

value 2.037 Å is normal for the trivalent rhodium ion and in fairly good agreement with those reported for other rhodium(III) porphyrin derivatives characterized by X-ray diffraction (e.g., 2.038 (6) Å in the octahedral complex bis(dimethylamine)(etio(I)porphyrinato)rhodium chloride dihydrate,[34] 2.031 (5) Å in (octaethylporphyrinato)-methylrhodium,[33] and 2.036 (3) Å in (octaethylporphyrin)rhodium–(octaethylporphyrin)indium).[35] In the last two complexes, the rhodium atom displays a square-pyramidal coordination geometry.

The 24-atom core of the porphyrinato moiety is only slightly distorted from planarity, and the largest deviations of atoms from the plane of best fit are 0.09–0.11 Å. The metal atom lies in the plane of the four pyrrole nitrogens, which are coplanar within 0.004 Å, and departs by only 0.022 Å from the mean plane of the 24-atom core. The pyrrole rings are planar to 0.024 Å and inclined 1.8–5.5 Å to the plane of the four coordinated nitrogens. The rhodium atom deviates up to 0.17 Å from the pyrrole mean planes. The four six-membered chelation rings are planar within experimental error. The 24-atom core mean plane makes angles of 95.6 (2), 100.6 (2), 85.9 (2), and 95.6 (2)° with the planes formed by the peripheral phenyl rings. As can be inferred from Table II, bond parameters within the porphinato system are normal and close to those found in other metal–porphyrin complexes.

The carbon atom of the carbene ligand is bonded to the rhodium atom at a distance of 2.030 (11) Å. Substantially shorter Rh–C bonds are found in other rhodium(III) compounds containing carbene ligands, namely, 1.930 (6) Å in $RhCl(PhCONCS)_2(PPh_3)_2(C_2H_5)_2O$,[36] 1.968 (13) Å in $I_3(OC)Rh–CPh(NMe)CPh{:}NMe$,[37] and 1.961 (11) Å in $RhCl_3(PEt_3)_2(CHNMe_2)$.[38] The hybridization of the carbene carbon atom is clearly sp^2, as indicated by the planarity of the RhCNN system and the bond angles at carbon, all close to the expected 120°. Within the carbene moiety, the two halves having C(53) in common are twisted with respect to one another by 133.9 (3)°. The central C(54)N(6)C(53)N(7)C(61) system is almost planar (+0.06 Å), and its mean plane makes dihedral angles of ca. 75° with both peripheral rings.

The isocyanide ligand bonds terminally to the metal atom in a slightly, but significantly, bent fashion, presumably as the result of packing forces in the crystal. Contrary to what is observed in most isocyanide complexes, the deviation from linearity is considerably higher at the carbon atom than at nitrogen, the bends being 10.4 and 2.1°, respectively. The $Rh–C_{isocyanide}$ distance of 2.064 (13) Å is relatively long when compared to those, 1.985 (7) and 1.993 (6) Å, reported for $[Rh(4\text{-}MeC_6H_4NC)_4I_2]^+$,[39] the only other crystallographically studied (isocyanide)rhodium (III) derivative of which we are aware.

The lengthening of the two Rh–C distances in the present structure is fully consistent with the trans effect shown by both the carbene and isocyanide ligands, which are trans to one another.

The molecular packing is dominated by van der Waals type interactions. The shortest non-hydrogen contact is 3.23 (2) Å between C(46) of the asymmetric unit and F(3) at $1 - x$, y, $1 - z$ position.

Extensive use of the Cambridge Crystallographic Database Files has been made for the bibliographic search.

Acknowledgment. Many thanks are due to P. Cutraro for his valuable technical assistance. We gratefully acknowledge the MPI (40%) for financial support.

Registry No. $[(OEP)Rh(CNBz)_2PF_6]$, 117559-08-7; $[(TPP)Rh(CNBz)_2PF_6]$, 117526-49-5; $[(OEP)Rh(CN\text{-}p\text{-}ClPh)_2PF_6]$, 117559-10-1; $[(TPP)Rh(CN\text{-}p\text{-}ClPh)_2PF_6]$, 117526-51-9; $[(TPP)Rh(t\text{-}BuNC)_2PF_6]$, 108638-55-7; $[(TPP)Rh(CO_2CH_3)]$, 69509-34-8; $[(OEP)Rh(CO_2CH_3)]$, 117526-56-4; $[(TPP)RhCH_3]$, 103562-25-0; $[(OEP)RhCH_3]$, 36643-85-3; [(TPP)Rh(Bz)], 117526-55-3; $PhCH_2NC$, 10340-91-7; $\{(TPP)Rh[{:}C(NHCH_2Ph)_2]PF_6\}$, 117526-39-3; $\{(OEP)Rh[{:}C(NHCH_2Ph)_2]PF_6\}$, 117559-02-1; $\{(TPP)Rh[{:}C(NHBz)_2](CNBz)PF_6\}$, 117526-41-7; $\{(TPP)Rh[{:}C(NHBz)_2][P(OMe)_3]PF_6\}$, 117526-43-9; $\{(TPP)Rh[{:}C(NHBz)_2](PPh_3)PF_6\}$, 117526-45-1; $\{(OEP)Rh[{:}C(NHBz)_2][P(OMe)_3]PF_6\}$, 117559-04-3; $\{(TPP)Rh[{:}C(NH\text{-}p\text{-}ClPh)_2]PF_6\}$, 117559-06-5; $\{(OEP)Rh[{:}C(NH\text{-}p\text{-}ClPh)_2]PF_6\}$, 117526-47-3; [(TPP)Rh(CONH-*t*-Bu)], 117526-52-0; [(OEP)Rh(CONH-*t*-Bu)], 117526-53-1; [(OEP)Rh(CONHBz)], 117526-54-2.

Supplementary Material Available: Tables of bond distances and angles, H-atom coordinates, and thermal parameters (11 pages); a listing observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(33) Takenaka, A.; Syal, S. K.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z. *Acta Crystallogr.* **1976**, *B32*, 62.

(34) Hanson, L. K.; Gouterman, M.; Hanson, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 4822.

(35) Jones, N. L.; Carrol, P. J.; Wayland, B. B. *Organometallics* **1986**, *5*, 33.

(36) Cowie, M.; Ibers, J. A. *Inorg. Chem.* **1971**, *15*, 552.

(37) Hitchcock, P. B.; Lappert, M. F.; McLaughlin, G. M.; Oliver, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 68.

(38) Cetinkaya, B.; Lappert, M. F.; McLaughlin, G. M.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1974**, 1591.

(39) Matsubayashi, G.; Inuma, T.; Tanaka, T.; Oka, K.; Nakatsu, K. *Inorg. Chim. Acta* **1985**, *102*, 145.