Photochemical Reactions of Tricarbonyl[hydrotris(1-pyrazolyl)borato]rhenium(I) in the Presence of Neutral Donor Ligands. *X*-Ray Crystal Structures of the Substitution Derivatives [Re{HB(pz)$_3$}(CO)$_2$L], with L = C_4H_8O or PPh_3 *

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The complex [Re{HB(pz)$_3$}(CO)$_3$] [HB(pz)$_3$ = hydrotris(1-pyrazolyl)borate] has been prepared. Ultraviolet irradiation of its tetrahydrofuran (thf) solution gave [Re{HB(pz)$_3$}(CO)$_2$(thf)], which allowed the synthesis of a series of substitution derivatives [Re{HB(pz)$_3$}(CO)$_2$L], with L = MeCN, $C_6H_{11}NC$, C_5H_5N, PMe_2Ph, or PPh_3. The reaction with 1,3-bis(diphenylphosphino)propane gave two species: one belongs to the previous family (diphosphine acting as a monodentate ligand), while the other is a dinuclear species, with the diphosphine bridging two Re[HB(pz)$_3$](CO)$_2$ units. The derivatives with L = thf and PPh_3 have been characterized by single-crystal *X*-ray analyses: L = thf, monoclinic, space group $P2_1/n$, a = 10.275(2), b = 12.457(3), c = 14.836(3) Å, β = 102.85(1)°, Z = 4, and R = 0.016; L = PPh_3, monoclinic, space group $C2/c$, a = 31.122(5), b = 9.721(2), c = 18.797(4), β = 93.62(1)°, Z = 8, and R = 0.027. The central Re^I is octahedrally co-ordinated by a $[HB(pz)_3]^-$ tridentate ligand (av. Re–N 2.157 and 2.190 Å respectively), two carbonyl ligands (av. Re–C 1.872 and 1.878 Å), and a thf or a PPh_3 ligand [Re–O 2.172(2), Re–P 2.387(2) Å].

The structural and electronic similarity between complexes containing η^5-cyclopentadienide (cp) and those containing poly(1-pyrazolyl)borate anions has been already pointed out.[1] Recently it was shown that the complexes [Rh{HB(3,5Me$_2$-pz)$_3$}(CO)L] [HB(3,5Me$_2$-pz)$_3$ = tris(3,5-dimethyl-1-pyrazolyl)hydroborate, L = CO[2] or C_2H_4[3]] are able photochemically to activate C–H bonds, in a manner analogous to that reported for cyclopentadienide complexes of Rh and Ir.[4] Taking into account that efficient photochemical C–H bond activation has been reported for [Re(cp)L$_3$] complexes,[5] we decided to investigate the photochemical reactivity of poly(1-pyrazolyl)borate complexes of rhenium.

Results and Discussion

The synthesis of the complex [Re{HB(3,5Me$_2$-pz)$_3$}(CO)$_3$], by reaction of K[HB(3,5Me$_2$-pz)$_3$] with [Re$_2$(μ-Cl)$_2$(CO)$_8$] has been reported[6] but nothing is known about its reactivity. Since the presence of the methyl substituents in the 3 and 5 positions of the pyrazole rings could result in significant steric hindrance, as observed for related manganese complexes,[7] we have prepared, by the same method, the unsubstituted pyrazolyl complex [Re{HB(pz)$_3$}(CO)$_3$] (**1**) [HB(pz)$_3$ = hydrotris(1-pyrazolyl)borate].

Irradiation of a diluted tetrahydrofuran (thf) solution of compound (**1**) with a high-pressure mercury lamp caused the solution to become yellow. I.r. monitoring showed the complete disappearance of the starting material in about 30 min, due to the substitution of one carbonyl by a solvent molecule, leading to the species [Re{HB(pz)$_3$}(CO)$_2$(thf)] (**2**), characterized on the basis of its spectroscopic data (Table 1), elemental analysis, and chemical reactivity. Eventually an *X*-ray single-crystal determination gave full support to the formulation.

It is noteworthy that the use of Pyrex-filtered radiation caused the reaction rate to become extremely low, in agreement with the position of the lowest-energy electronic absorption band of (**1**), at 282 nm.

Care must be taken to keep the reaction temperature at about 0 °C and the irradiation time as low as possible: at room temperature or in the case of prolonged photolysis the irradiated solutions acquire a red-brown colour, due to the formation of unidentified species which no longer contain carbonyl ligands. It is not possible, therefore, in this way to synthesize the product of substitution of a second carbonyl by thf.

As expected, the co-ordinated solvent molecule is rather substitution labile and compound (**2**) in solution is stable only in thf. In non-co-ordinating solvents, such as dichloromethane or benzene, slow decomposition was observed, as evidenced by the darkening of the solution and the appearance of a number of bands in the ν(CO) region of the i.r. spectrum. In co-ordinating media, on the other hand, a solvent molecule replaced the thf: in ethanol a compound still more unstable was formed, whilst the derivative (**3**) obtained in acetonitrile was stable also in non-co-ordinating solvents.

Compound (**2**) allowed the synthesis of a variety of substitution derivatives of general formula [Re{HB(pz)$_3$}(CO)$_2$L], where L is a two-electron donor molecule: PPh_3, (**4**); PMe_2Ph, (**5**); NC_5H_5, (**6**); or CNC_6H_{11}, (**7**). Due to the instability of (**2**) in non-co-ordinating solvents, the substitution reactions were accomplished directly in thf solution, at 60 °C, using a ten-fold excess of L. The rate of the substitution decreased in the order isonitrile > phosphines > pyridine ($t_{\frac{1}{2}}$ ranging from 30 to 90 min), indicating that the π-acceptor ability is more important than the σ donicity. This is just what should be expected, taking into account that the substitutions occur in *trans* to a strong donor group such as the tris(pyrazolyl)borate.

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* Dicarbonyl(tetrahydrofuran)- and dicarbonyl(triphenylphosphine)-[hydrotris(1-pyrazolyl)borato]rhenium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Spectroscopic data for the compounds $[Re\{HB(pz)_3\}(CO)_2L]$. I.r. spectra were recorded in tetrahydrofuran solution, n.m.r. spectra in $CDCl_3$. The primed positions refer to the pyrazole rings *trans* to the ligand L. The signals for 4 and 4′ are triplets, the others doublets or doublets of doublets (coupling constants in Hz are in parentheses)

			^{1}H N.m.r. (pyrazolic hydrogens)					
	Ligand	I.r., ν(CO)/ cm^{-1}	3	3′	5	5′	4	4′
(1)	CO	2 024, 1 914	7.82 (2.1)		7.65 (2.4) (0.6)		6.21 (2.2)	
(2)	thf[a]	1 907, 1 823	7.82 (1.8)	7.43 (1.7)	7.73 (2.3)	7.54 (2.8)	6.27 (2.2)	6.02 (2.2)
(3)	MeCN[b]	1 920, 1 841	7.78 (1.9)	7.72 (2.1)	7.66 (2.3) (0.6)	7.58 (2.4)	6.23 (2.2)	6.11 (2.2)
(4)	PPh_3[c]	1 927, 1 850	6.73 (1.8)	7.93 (2.0)	7.61 (2.2)	7.56 (2.6)	5.82 (2.2)	6.16 (2.2)
(5)	PMe_2Ph[d]	1 922, 1 844	7.19 (2.0)	7.86 (2.1)	7.62 (2.4)	7.53 (2.4)	6.02 (2.2)	6.11 (2.2)
(6)	NC_5H_5[e]	1 907, 1 828	7.34 (2.0)	7.80 (1.9)	7.73 (2.3)	7.59 (2.5)	6.20 (2.2)	6.13 (2.2)
(7)	CNC_6H_{11}[f]	1 931, 1 869	7.78 (1.8)	7.85 (2.1)	7.63 (2.2) (0.6)	7.6[g]	6.18 (2.2)	6.16 (2.2)
(8)	dppp[h]	1 923, 1 846	6.85 (1.7)	7.90 (1.6)	7.5[i]	7.5[i]	5.80 (2.2)	6.14 (2.2)
(9)	μ-dppp[j]	1 923, 1 846	6.81 (2.1)	7.88 (1.9)	7.5[i]	7.5[i]	5.79 (2.2)	6.13 (2.2)

[a] Co-ordinated thf: 3.77 (4, m) and 1.81 (4, m). [b] Co-ordinated acetonitrile: 2.50 (3, s). [c] Co-ordinated triphenylphosphine: 7.27 (15, m). [d] Co-ordinated dimethylphenylphosphine: 7.31 (5, m) and 1.95 (6, d, J_{HP} 9 Hz). [e] Co-ordinated pyridine: 8.29 (2, m), 7.53 (1, tt), and 6.99 (2, m). [f] Co-ordinated *cyclo*hexylisocyanide: 3.92 (1, m), 1.81 (4, m), and 1.55 (6, m). [g] The signal partially overlaps with that of H(5). [h] Co-ordinated dppp: 7.25 (20, m), 2.86 (2, m), 2.19 (2, m), and 1.62 (2, m). [i] The signals partially overlap with those of the phenyls of the phosphine. [j] The compound has the formula $[\{Re[HB(pz)_3](CO)_2\}_2(\mu\text{-dppp})]$. Co-ordinated dppp: 7.16 (20, m), 2.89 (4, m), and 1.60 (2, m).

In spite of being a good π acceptor, carbon monoxide was not able to replace the thf ligand, when bubbled through a thf solution of compound (**2**). Using benzene as solvent, the substitution occurred, in about 5 h at room temperature; but also in this case some unidentified by-product was formed.

The direct synthesis of the $[Re\{HB(pz)_3\}(CO)_2L]$ complexes was attempted, by irradiation of (**1**) in thf solution in the presence of an excess of L. However, also under these conditions, only compound (**2**) was formed. This result was quite surprising, taking into account that donor groups L are able to replace the co-ordinated solvent molecule, even in thf solution. However it was rationalized when it was shown that the irradiation of a thf solution of compound (**4**) gave (**2**) selectively, indicating that the phosphine ligand is photolabilized much easier than a carbonyl. This implies also that disubstituted derivatives cannot be prepared through this route.

The use of toluene as solvent was then attempted, irradiating compound (**1**) in the presence of 10 equivalents of PPh_3, but the reaction resulted in poor selectivity, the expected compound (**4**) being accompanied by other unidentified products. Also in the case of the related complex $[Re(cp)(CO)_3]$, the synthesis of the derivatives $[Re(cp)(CO)_2L]$ was better accomplished *via* the thf derivative, rather than by direct irradiation.[8]

The reaction of (**2**) with a slight excess of $Ph_2P(CH_2)_3PPh_2$ (dppp) resulted in the formation of two derivatives, exhibiting identical i.r. spectra in the carbonyl region. They were separated by chromatography and characterized spectroscopically. The species first eluted was formulated as $[Re\{HB(pz)_3\}(CO)_2(dppp)]$ (**8**), with the diphosphine acting as a monodentate ligand. The electron-impact (e.i.) mass spectrum showed the molecular-ion multiplet centred at *m*/*z* 867, and two resonances were present in the ^{31}P n.m.r. spectrum, one at 18.29 p.p.m., attributable to the phosphorus atom co-ordinated to rhenium and the other one at −17.38 p.p.m., a value comparable with that[9] of the free dppp ligand (−17.3 p.p.m.). Moreover in the ^1H n.m.r. spectrum the integrated intensities indicated the presence of one dppp ligand for each pyrazolylborate anion.

The second compound was formulated as the dimeric species $[\{Re[HB(pz)_3](CO)_2\}_2(\mu\text{-dppp})]$ (**9**), with the diphosphine acting as a bridge between the two rhenium atoms. The molecular-ion multiplet in the e.i. mass spectrum was centred at *m*/*z* 1 322 (with the isotopic pattern expected for a Re_2 species), only one signal (17.88 p.p.m.) was present in the ^{31}P n.m.r. spectrum, and the ^1H n.m.r. spectrum showed a 0.5:1 ratio of dppp to pyrazolylborate.

In accord with these formulations, it was possible to synthesize selectively compound (**9**) using 0.5 equivalent of dppp: i.r. and t.l.c. monitoring showed that at first a mixture of (**8**) and (**9**) [plus some unreacted (**1**)] formed, which slowly rearranged, leading eventually (about 16 h, in boiling thf) to pure (**9**). On the contrary, the use of a more diluted solution of (**1**) (about 1/10) and a six-fold excess of dppp gave (**8**) as the main species, but still contaminated by some (**9**).

As to the possibility of hydrocarbon C–H bond activation, we irradiated compound (**1**) at 0 °C in toluene in the absence of donor species L: under these conditions oxidative addition of the solvent or dimerization is expected. Indeed, some reaction occurred, as indicated by spectroscopic monitoring, but to date we have not been able to characterize the products, possibly due to their thermal instability. Work is still in progress, involving also the use of complexes soluble in saturated hydrocarbons, such as the phosphine derivative (**5**) or the analogue of (**1**) containing the $HB(3,5Me_2\text{-}pz)_3$ ligand.

Spectroscopic Data.—The carbonyl stretching region of the i.r. spectra of compounds (**1**)—(**9**) consists of two bands (Table 1). The trend of the ν(CO) frequencies is in line with the expected shift to lower frequencies caused by the substitution of one carbon monoxide by a ligand of lower π acidity. In particular, the difference between the frequencies observed for compounds (**4**) and (**5**) is slightly higher than that between the corresponding Tolman electronic parameters, ν.[9] The values of the carbonyl stretching frequencies of compounds (**1**) and (**4**) are lower than those reported for the corresponding cyclopentadienide complexes:[8,10] this suggests that $HB(pz)_3$ is a better donor than cp and more comparable, also from the steric point of view, with C_5Me_5.[11]

The ^1H n.m.r. spectra exhibit two signals (ratio 2:1) for each of the positions 3—5 of the pyrazole rings (Table 1), in agreement with the idealized C_s symmetry imposed by the ligand L. This implies the absence in solution at room temperature either of free rotation of the pyrazolylborate ligand or of scrambling between the carbonyls and the L ligands. An

Table 2. Selected bond distances (Å) and angles (°) within compounds (**2**) and (**4**)

	Compound (**2**)	Compound (**4**)		Compound (**2**)	Compound (**4**)
Re–C(1)	1.881(4)	1.872(8)	N(2A)–C(2A)	1.346(5)	1.350(9)
Re–C(2)	1.863(4)	1.883(8)	N(2B)–C(2B)	1.343(5)	1.342(9)
Re–N(1B)	2.105(3)	2.155(5)	C(2A)–C(2C)	1.351(6)	1.356(11)
Re–N(2B)	2.169(3)	2.204(5)	C(2B)–C(2C)	1.377(6)	1.383(10)
Re–N(3B)	2.197(3)	2.212(5)	N(3A)–N(3B)	1.355(4)	1.347(7)
Re–O	2.172(2)		N(3A)–C(3A)	1.356(5)	1.343(8)
Re–P		2.387(2)	N(3B)–C(3B)	1.336(5)	1.347(8)
C(1)–O(1)	1.155(5)	1.169(9)	C(3A)–C(3C)	1.353(7)	1.368(11)
C(2)–O(2)	1.177(4)	1.149(8)	C(3B)–C(3C)	1.382(6)	1.385(10)
B–N(1A)	1.545(5)	1.511(10)	O–C(3)	1.440(6)	
B–N(2A)	1.541(5)	1.540(10)	C(3)–C(4)	1.475(6)	
B–N(3A)	1.534(5)	1.560(9)	C(4)–C(5)	1.499(8)	
N(1A)–N(1B)	1.372(4)	1.349(7)	C(5)–C(6)	1.471(7)	
N(1A)–C(1A)	1.361(5)	1.353(9)	C(6)–O	1.418(5)	
N(1B)–C(1B)	1.339(4)	1.330(9)	P–C(11)		1.826(7)
C(1A)–C(1C)	1.365(6)	1.346(11)	P–C(21)		1.851(7)
C(1B)–C(1C)	1.379(6)	1.375(11)	P–C(31)		1.837(7)
N(2A)–N(2B)	1.366(4)	1.349(7)			
C(1)–Re–C(2)	88.5(2)	87.4(3)	C(1A)–C(1C)–C(1B)	105.8(4)	104.5(8)
C(1)–Re–N(1B)	96.2(1)	90.4(3)	Re–N(2B)–N(2A)	120.1(2)	120.3(5)
C(1)–Re–N(2B)	176.9(1)	173.7(3)	Re–N(2B)–C(2B)	133.4(3)	133.6(5)
C(1)–Re–N(3B)	93.0(1)	96.4(3)	B–N(2A)–N(2B)	119.4(3)	120.1(6)
C(1)–Re–O	95.1(1)		B–N(2A)–C(2A)	132.5(4)	131.4(7)
C(1)–Re–P		93.5(2)	N(2B)–N(2A)–C(2A)	108.1(3)	108.5(6)
C(2)–Re–N(1B)	93.6(1)	92.1(3)	N(2A)–N(2B)–C(2B)	106.4(3)	106.1(6)
C(2)–Re–N(2B)	94.6(1)	92.0(3)	N(2A)–C(2A)–C(2C)	110.1(4)	110.5(7)
C(2)–Re–N(3B)	177.4(1)	171.9(3)	N(2B)–C(2B)–C(2C)	110.5(4)	111.6(7)
C(2)–Re–O	94.5(1)		C(2A)–C(2C)–C(2B)	104.9(4)	103.3(7)
C(2)–Re–P		95.2(2)	Re–N(3B)–N(3A)	119.6(2)	119.9(4)
N(1B)–Re–N(2B)	84.1(1)	83.4(2)	Re–N(3B)–C(3B)	133.0(3)	134.0(5)
N(1B)–Re–N(3B)	84.1(1)	80.7(2)	B–N(3A)–N(3B)	119.9(3)	119.9(5)
N(2B)–Re–N(3B)	83.9(1)	83.5(2)	B–N(3A)–C(3A)	130.9(3)	129.9(6)
N(1B)–Re–O	166.3(1)		N(3B)–N(3A)–C(3A)	109.0(3)	109.9(6)
N(1B)–Re–P		171.9(2)	N(3A)–N(3B)–C(3B)	107.0(3)	106.1(6)
N(2B)–Re–O	84.3(1)		N(3A)–C(3A)–C(3C)	108.1(4)	109.0(7)
N(2B)–Re–P		92.8(2)	N(3B)–C(3B)–C(3C)	109.5(4)	110.5(7)
N(3B)–Re–O	87.5(1)		C(3A)–C(3C)–C(3B)	106.3(4)	104.5(7)
N(3B)–Re–P		91.7(1)	Re–O–C(3)	127.6(2)	
Re–C(1)–O(1)	178.6(4)	173.1(7)	Re–O–C(6)	123.2(3)	
Re–C(2)–O(2)	178.5(3)	173.9(7)	O–C(3)–C(4)	104.8(4)	
N(1A)–B–N(2A)	108.3(3)	110.2(6)	C(3)–C(4)–C(5)	104.2(4)	
N(1A)–B–N(3A)	107.7(3)	108.3(6)	C(4)–C(5)–C(6)	104.4(4)	
N(2A)–B–N(3A)	108.6(3)	107.2(6)	C(5)–C(6)–O	107.9(4)	
Re–N(1B)–N(1A)	119.7(2)	121.6(4)	C(6)–O–C(3)	109.2(3)	
Re–N(1B)–C(1B)	133.9(3)	132.3(5)	Re–P–C(11)		113.6(2)
B–N(1A)–N(1B)	121.3(3)	120.2(6)	Re–P–C(21)		115.5(2)
B–N(1A)–C(1A)	129.9(4)	130.9(7)	Re–P–C(31)		118.5(2)
N(1B)–N(1A)–C(1A)	108.8(3)	108.8(6)	C(11)–P–C(21)		102.3(3)
N(1A)–N(1B)–C(1B)	106.4(3)	106.0(6)	C(11)–P–C(31)		101.9(3)
N(1A)–C(1A)–C(1C)	108.4(4)	109.3(8)	C(21)–P–C(31)		102.8(3)
N(1B)–C(1B)–C(1C)	110.6(4)	111.3(7)			

analogous stereochemical rigidity was observed [12] in the related complexes $[\mathrm{Mn\{HB(3,5Me_2\text{-}pz)_3\}(CO)_2L}]$ $[\mathrm{L} = \mathrm{P(OMe)_3}$, $\mathrm{P(OPh)_3}$, or $\mathrm{PMe_3}]$, but not in the corresponding compounds $[\mathrm{Mn\{B(pz)_4\}(CO)_2L}]$. This was rationalized assuming that the steric hindrance of the methyl groups in the pyrazole rings inhibits free rotation of the pyrazolylborate anion. In the present case, however, we observe the same rigidity even in the absence of the methyl groups.

The assignments of the resonances of the hydrogens at positions 3—5 of the pyrazole rings (Table 1) have been based mainly on the values of the coupling constants $[J(\mathrm{H^4H^5}) > J(\mathrm{H^3H^4})]$.[13] Another useful feature, in some of these compounds, is the additional low coupling constant (0.6 Hz) exhibited by the hydrogens in position 5, which can be attributed to coupling with the hydrogen bound to boron.

Description of the Structures of Compounds (**2**) *and* (**4**).—The crystals of compounds (**2**) and (**4**) consist of a packing of discrete neutral molecules. The overall structures are apparent from the ORTEP drawings (Figures 1 and 2, respectively); relevant bond parameters are reported in Table 2.

In both compounds the rhenium atom is in a distorted octahedral environment in which the $[\mathrm{HB(pz)_3}]^-$ ligand chelates one face of the octahedron; the remaining sites are occupied by two carbonyl ligands and a thf (**2**) or a $\mathrm{PPh_3}$ (**4**) ligand. To our knowledge these compounds are the first examples of rhenium tris(1-pyrazolyl)borate complexes so far structurally characterized.

The $[\mathrm{HB(pz)_3}]^-$ ligand acts as a tridentate chelating group with idealized C_{3v} symmetry, the C_3 axis passing through the B atom and the metal. The Re–N bond distances are somewhat

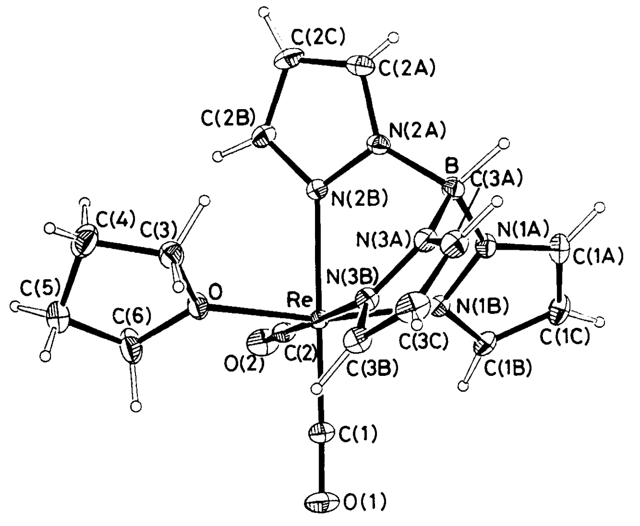

Figure 1. A view of [Re{HB(pz)$_3$}(CO)$_2$(thf)] (2), with atom labels

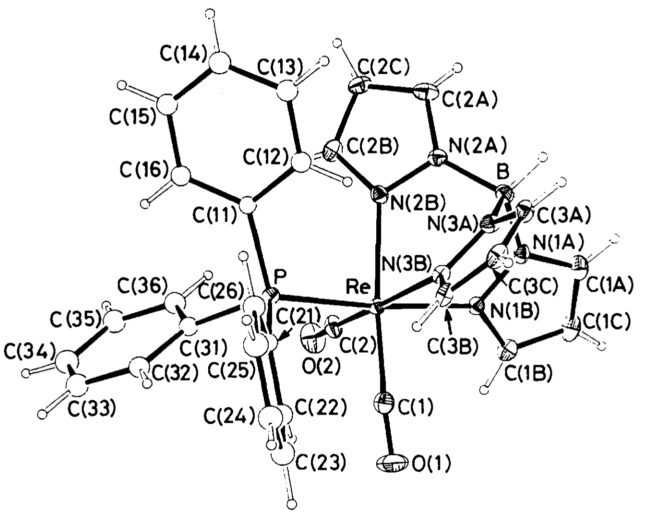

Figure 2. A view of [Re{HB(pz)$_3$}(CO)$_2$(PPh$_3$)] (4)

Table 3. Crystal data for [Re{HB(pz)$_3$}(CO)$_2$(thf)] (2) and [Re{HB(pz)$_3$}(CO)$_2$(PPh$_3$)] (4)[a]

Compound	(2)	(4)
Formula	$C_{15}H_{18}BN_6O_3Re$	$C_{29}H_{25}BN_6O_2PRe$
M	527.36	717.55
a/Å	10.275(2)	31.122(5)
b/Å	12.457(3)	9.721(2)
c/Å	14.836(3)	18.797(4)
β/°	102.85(1)	93.62(1)
U/Å^3	1 851.4	5 675.4
Z, D_c/g cm^{-3}	4, 1.89	8, 1.68
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
F(000)	1 016	2 816
μ(Mo-K_α)/cm^{-1}	66.78	44.31
2θ range/°	$6 \leqslant 2\theta \leqslant 50$	$6 \leqslant 2\theta \leqslant 48$
Scan interval/°	0.9 + 0.347 tanθ	0.8 + 0.347 tanθ
No. of data collected[b]	3 273	4 736
No. of data used [$I > 3\sigma(I)$]	2 637	2 804
Max., min. transmission factors	1.00, 0.66	1.00, 0.93
Crystal size/mm	0.25 × 0.25 × 0.17	0.13 × 0.08 × 0.06
R	0.0160	0.0273
R'	0.0208	0.0286
E.s.d.	1.083	1.100
No. variable parameters	299	301
Max. peak in final difference Fourier/ e Å^{-3}	0.85	0.52

[a] Details in common: crystal system, monoclinic; graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å); ω scan method; prescan speed 16° min^{-1}; collected octants $\pm h,k,l$; weighting factor $p = 0.03$; e.s.d. = $[\Sigma w(|F_o| - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o = number of observations and N_v = number of variables; $w = 4|F_o|^2/\sigma^2(|F_o|^2)$ where $\sigma(|F_o|^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/L_p$ and L_p = Lorentz polarization factor; $R = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] Room temperature.

scattered, those *trans* to the Re–C–O linkages being significantly larger than the one *trans* to the oxygen or phosphorus atom (see Table 2). This could be indicative of a weaker Re–L (L = thf or PPh$_3$) interaction with respect to the Re–CO ones. All the Re–N bond lengths within compound (4) are systematically longer than the corresponding ones in compound (2), probably owing to the greater steric hindrance of the PPh$_3$ ligand. The other bond distances and angles within the [HB(pz)$_3$]$^-$ moiety are similar to those observed in related systems.[1]

The molecular parameters of the thf, PPh$_3$, and CO ligands are normal. In compound (2) the Re–O bond distance is in agreement with the values observed in other rhenium compounds.[14,15] The oxygen is nearly trigonally co-ordinated with the Re atom 0.019 Å apart from the O,C(3),C(6) plane. The five-membered ring displays an envelope conformation with C(4) 0.456(5) Å out of the mean plane of the other atoms (maximum deviation from planarity 0.025 Å); the dihedral angle between the C(3),C(4),C(5) fragment and the plane defined by the O,C(3),C(5),C(6) atoms is 30.0°. The mean plane of the thf ligand is rotated relative to the Re,N(1B),N(3B),C(2) and Re,N(2B),N(3B),C(1) mean planes by 41.6 and 48.6°, respectively.

In compound (4) the presence of the triphenylphosphine group causes a small departure from the linearity of the Re–C–O bonds [173.4° (av.)] with the CO groups tilted away from the phenyl rings.

Experimental

All reactions were carried out under a nitrogen atmosphere in solvents deoxygenated and dried by standard methods. The i.r. spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer and the n.m.r. spectra on a Bruker W.P. 80 spectrometer. The irradiations were performed with a Philips H.P.K. 125-W, high-pressure mercury lamp, immersed in a quartz refrigerator, in turn immersed in the reaction vessel. Potassium hydrotris(1-pyrazolyl)borate was prepared by the method of Trofimenko.[16] The compound [Re$_2$(μ-Cl)$_2$(CO)$_8$] was prepared by a literature method.[17] Triphenylphosphine (Merck), dimethylphenylphosphine (Strem), and cyclohexyl isocyanide (Aldrich) were used without further purification. 1,3-Bis(diphenylphosphino)propane (dppp) (Merck) was recrystallized from methanol. Pyridine (Merck) and acetonitrile (Merck) were purified before the use by standard methods.

Preparation of the Compounds.—[Re{HB(pz)$_3$}(CO)$_3$] (1). Compound (1) was prepared using a method similar to that reported[6] for [Re{HB(3,5Me$_2$-pz)$_3$}(CO)$_3$]: a solution of [Re$_2$(μ-Cl)$_2$(CO)$_8$] (0.67 g, 1 mmol) in thf (40 cm^3) was treated at room temperature with K[HB(pz)$_3$] (0.504 g, 2 mmol). After 2 h the solution was filtered and evaporated under reduced

Table 4. Positional parameters and their estimated standard deviations (e.s.d.s) within compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.026 86(1)	0.135 86(1)	0.238 12(1)	C(2A)	−0.213 4(4)	0.217 9(3)	0.428 3(3)
O(1)	0.151 5(3)	0.117 2(2)	0.071 5(2)	C(2B)	−0.020 7(4)	0.140 8(3)	0.446 9(3)
O(2)	0.129 5(3)	−0.088 9(2)	0.293 5(2)	C(2C)	−0.113 5(5)	0.176 6(4)	0.494 1(3)
C(1)	0.102 8(4)	0.123 5(3)	0.134 4(3)	N(3A)	−0.181 8(3)	0.319 6(2)	0.205 2(2)
C(2)	0.089 6(4)	−0.001 7(3)	0.273 3(2)	N(3B)	−0.056 3(3)	0.295 5(2)	0.196 9(2)
B	−0.262 8(4)	0.236 9(3)	0.246 4(3)	C(3A)	−0.216 6(4)	0.417 0(3)	0.166 5(3)
N(1A)	−0.275 4(3)	0.134 8(2)	0.186 0(2)	C(3B)	−0.013 2(4)	0.378 6(3)	0.154 6(3)
N(1B)	−0.164 6(3)	0.081 5(2)	0.172 2(2)	C(3C)	−0.112 8(5)	0.455 1(3)	0.133 7(3)
C(1A)	−0.386 4(4)	0.084 0(3)	0.137 6(3)	O	0.197 7(2)	0.216 7(2)	0.323 7(2)
C(1B)	−0.209 5(4)	−0.001 0(3)	0.116 0(2)	C(3)	0.199 5(4)	0.318 3(3)	0.370 2(3)
C(1C)	−0.347 1(4)	−0.002 2(3)	0.093 5(3)	C(4)	0.319 6(5)	0.314 2(4)	0.446 2(3)
N(2A)	−0.184 6(3)	0.207 8(2)	0.344 6(2)	C(5)	0.414 9(5)	0.244 6(4)	0.409 4(3)
N(2B)	−0.062 9(3)	0.159 2(2)	0.355 9(2)	C(6)	0.328 5(5)	0.173 3(4)	0.342 8(4)

pressure. The oil residue was washed with methanol and a white solid was obtained (0.590 g, 61%), m.p. 277 °C (Found: C, 29.75; H, 2.10; N, 17.00. $C_{12}H_{10}BN_6O_3Re$ requires C, 29.80; H, 2.05; N, 17.40%). ν(BH) 2 540w, ν(CO) 2 013s and 1 890vs cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(thf)] (**2**). A solution of complex (**1**) (0.100 g, 0.21 mmol) in thf (80 cm^3) was irradiated at 0 °C for 30 min. It gradually turned yellow. Upon reduction of the volume of solvent in vacuum to 2 cm^3, addition of ethanol (10 cm^3) produced a yellow microcrystalline precipitate (0.052 g, 48%). The sample used for the *X*-ray crystal analysis was obtained by slow evaporation of a thf solution of complex (**2**) at −20 °C, m.p. 124 °C (decomp.) (Found: C, 34.50; H, 3.40; N, 15.40. $C_{15}H_{18}BN_6O_3Re$ requires C, 34.15; H, 3.40; N, 15.95%). ν(BH) 2 488w, ν(CO) 1 896s, 1 814s, and 1 799s cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(MeCN)] (**3**). Complex (**2**) (0.050 g, 0.095 mmol) was dissolved in acetonitrile (20 cm^3). The solution was stirred for 8 h at room temperature, with i.r. monitoring, then the volume was reduced under vacuum and ethanol added, giving a white crystalline product (0.040 g, 85%), m.p. 190 °C (decomp.) (Found: C, 31.30; H, 2.60; N, 19.50. $C_{13}H_{13}BN_7O_2Re$ requires C, 31.45; H, 2.60; N, 19.75%). ν(BH) 2 564w, ν(CO) 1 905s, 1 825s, 1 808s, and ν(CN) 2 264m cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(PPh$_3$)] (**4**). To a thf solution (20 cm^3) of triphenylphosphine (0.063 g, 1.2 mmol), complex (**2**) (0.313 g, 0.12 mmol) was added. The solution was heated for 5 h at 60 °C. After reduction of the volume of the solvent in vacuum, a white solid was precipitated by addition of ethanol (0.060 g, 70%). The sample used for the *X*-ray crystal-structure determination was obtained by slow diffusion of n-hexane into a cyclohexane solution of complex (**4**), m.p. > 250 °C (Found: C, 48.20; H, 3.55; N, 11.50. $C_{29}H_{25}BN_6O_2PRe$ requires C, 48.55; H, 3.50; N, 11.70%). ν(BH) 2 516w, ν(CO) 1 917s, 1 842s, and 1 832s cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(PMe$_2$Ph)] (**5**). This complex was prepared as described for (**4**), using 10 equivalents of PMe$_2$Ph (0.052 g, 73%), m.p. 187 °C (Found: C, 38.20; H, 3.50; N, 13.75. $C_{19}H_{21}BN_6O_2PRe$ requires C, 38.45; H, 3.55; N, 14.15%). ν(BH) 2 486w, ν(CO) 1 916s and 1 836s cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(NC$_5$H$_5$)] (**6**). This yellow complex was prepared as described for (**3**) (0.041 g, 81%), m.p. 181 °C (Found: C, 35.60; H, 2.70; N, 18.30. $C_{16}H_{15}BN_7O_2PRe$ requires C, 35.95; H, 2.80; N, 18.35%). ν(BH) 2 524w, ν(CO) 1 897s and 1 816s cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(CNC$_6$H$_{11}$)] (**7**). To a thf solution (20 cm^3) of complex (**2**) (0.063 g, 0.12 mmol), cyclohexyl isocyanide (0.131 g, 1.2 mmol) was added. The solution was heated for 3 h at 60 °C. Removal of solvent and chromatographic purification on a silica-gel column using dichloromethane–hexane (1:1) as the eluant gave the white crystalline product (0.027 g, 40%), m.p. 133 °C (Found: C, 38.10; H, 3.70; N, 17.15. $C_{18}H_{21}BN_7O_2Re$ requires C, 38.30; H, 3.70; N, 17.40%). ν(BH) 2 492w, ν(NC) 2 132m, ν(CO) 1 922s and 1 853s cm^{-1} (Nujol).

[Re{HB(pz)$_3$}(CO)$_2$(dppp)] (**8**). To a thf solution (50 cm^3) of complex (**2**) (0.060 g, 0.11 mmol) solid dppp (0.281 g, 0.68 mmol) was added. The solution was heated for 4 h at 60 °C. Removal of solvent and chromatographic purification on a silica-gel column using dichloromethane–hexane (1:1) as the eluant gave the white crystalline product (0.048 g, 49%), m.p. 80 °C (Found: C, 52.50; H, 4.10; N, 9.45. $C_{38}H_{36}BN_6O_2P_2Re$ requires C, 52.60; H, 4.15; N, 9.70%). ν(BH) 2 484w, ν(CO) 1 916s and 1 837s cm^{-1} (Nujol).

[{Re[HB(pz)$_3$](CO)$_2$}$_2$(μ-dppp)] (**9**). To a thf solution (5 cm^3) of complex (**2**) (0.060 g, 0.11 mmol) solid dppp (0.023 g, 0.06 mmol) was added. The solution was heated for 16 h at 60 °C. Upon reduction of the volume of the solvent in vacuum a white solid was precipitated by addition of ethanol (0.065 g, 86%), m.p. 151 °C (Found: C, 44.25; H, 3.30; N, 12.40. $C_{49}H_{46}B_2N_{12}O_4P_2Re_2$ requires C, 44.50; H, 3.50; N, 12.70%). ν(BH) 2 484w, ν(CO) 1 922s and 1 843s cm^{-1} (Nujol).

X-Ray Crystal Analyses of Compounds (**2**) *and* (**4**).—Crystal data and experimental conditions for both compounds are reported in Table 3. The intensity data were collected with an Enraf-Nonius CAD4 automated diffractometer. A least-squares fit of 25 randomly oriented reflections with θ ranging from 8 to 12° provided the unit-cell parameters. Three standard reflections were measured at regular intervals during the data collections and no decay was observed. Intensities were collected using a variable scan range with a 25% extension at each end for background determination. Correction for Lorentz and polarization effects was applied. An empirical absorption correction was performed based on ψ scans (ψ 0—360, every 10°) of three suitable reflections with χ values close to 90°.

Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares using the Enraf-Nonius structure determination package (SDP)[18] and the constants tabulated therein on a PDP 11/73 computer. The final values of the agreement indices are reported in Table 3.

Anisotropic thermal parameters were assigned to all non-hydrogen atoms in compound (**2**). The hydrogen atoms were all refined, with fixed isotropic thermal parameters only for the hydrogens belonging to the thf ligand (B = 7 Å^2). In compound (**4**) the non-hydrogen atoms were refined anisotropically with the exception of the phenyl carbon atoms. The hydrogen atoms of the [HB(pz)$_3$]$^-$ ligand were refined with fixed thermal parameters (B = 5 Å^2), while those bonded to the phenyl rings were located in their ideal positions (C–H 0.95 Å) after each

Table 5. Positional parameters and their e.s.d.s within compound (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.110 93(1)	0.299 39(3)	0.555 37(1)	C(3B)	0.151 3(2)	0.386 6(7)	0.715 2(4)
P	0.156 78(6)	0.106 3(2)	0.580 35(9)	C(3C)	0.137 2(3)	0.430 2(8)	0.780 0(4)
O(1)	0.180 1(2)	0.483 6(7)	0.499 8(4)	C(11)	0.133 4(2)	−0.023 2(7)	0.636 8(3)
O(2)	0.086 8(2)	0.233 2(7)	0.400 6(3)	C(12)	0.114 3(2)	0.020 7(8)	0.697 8(4)
C(1)	0.155 5(2)	0.408 2(8)	0.523 6(4)	C(13)	0.095 3(2)	−0.073 6(8)	0.741 8(4)
C(2)	0.097 5(2)	0.252 3(8)	0.459 4(4)	C(14)	0.095 1(2)	−0.211 4(9)	0.724 9(4)
B	0.037 0(3)	0.400(1)	0.661 0(4)	C(15)	0.113 9(2)	−0.256 5(8)	0.665 3(4)
N(1A)	0.039 2(2)	0.496 1(6)	0.598 1(3)	C(16)	0.133 2(2)	−0.163 2(7)	0.621 5(4)
N(1B)	0.068 0(2)	0.473 6(6)	0.548 7(3)	C(21)	0.208 6(2)	0.144 9(7)	0.630 2(3)
C(1A)	0.017 4(2)	0.613 5(9)	0.581 5(4)	C(22)	0.235 6(2)	0.239 3(8)	0.602 4(4)
C(1B)	0.063 8(2)	0.577 8(8)	0.502 9(4)	C(23)	0.274 6(3)	0.272 8(9)	0.639 0(4)
C(1C)	0.032 1(3)	0.667 2(8)	0.521 5(4)	C(24)	0.285 5(3)	0.214 2(9)	0.703 5(4)
N(2A)	0.027 6(2)	0.252 4(6)	0.635 1(3)	C(25)	0.259 3(3)	0.120(1)	0.731 9(4)
N(2B)	0.053 7(2)	0.190 8(6)	0.590 2(3)	C(26)	0.220 3(2)	0.083 4(8)	0.694 5(4)
C(2A)	−0.005 0(2)	0.165 5(9)	0.647 2(4)	C(31)	0.173 4(2)	0.001 7(8)	0.505 4(4)
C(2B)	0.036 5(2)	0.066 8(8)	0.575 4(4)	C(32)	0.215 4(2)	−0.039 9(8)	0.500 0(4)
C(2C)	−0.000 4(2)	0.045 8(8)	0.611 4(4)	C(33)	0.225 5(3)	−0.125 4(9)	0.442 8(4)
N(3A)	0.082 1(2)	0.398 5(6)	0.702 3(3)	C(34)	0.194 2(3)	−0.167 0(9)	0.394 0(4)
N(3B)	0.117 4(2)	0.367 6(6)	0.667 8(3)	C(35)	0.152 3(3)	−0.127 8(9)	0.398 9(4)
C(3A)	0.093 4(3)	0.436 2(8)	0.769 7(4)	C(36)	0.141 6(2)	−0.043 2(8)	0.454 5(4)

cycle but not refined. The peaks in the final difference Fourier maps of both compounds were randomly located.

The final values of the positional parameters for compounds (**2**) and (**4**) are reported in Tables 4 and 5, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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