Crystal and Molecular Structures of μ-Hydrido-bis[*fac*-(2,2′-bipyridine)-tricarbonylrhenium(I)] Chloride, *fac*-(2,2′-Bipyridine)tricarbonyl-formatorhenium(I), and *fac*-(2,2′- Bipyridine)tricarbonyl(cyanotri-hydroborato)rhenium(I) *

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The crystal and molecular structures of the compounds $[Re_2(bipy)_2(CO)_6(\mu\text{-}H)]Cl$ (**1**), *fac*-$[Re(bipy)(CO)_3(HCO_2)]$ (**2**), and *fac*-$[Re(bipy)(CO)_3\{BH_3(CN)\}]$ (bipy = 2,2′-bipyridine) have been determined by the heavy-atom method from three-dimensional *X*-ray data collected by counter methods. Compound (**1**) is triclinic and crystallizes in space group $P\bar{1}$, $Z = 2$, with cell constants $a = 18.848(9)$, $b = 10.171(5)$, $c = 8.449(4)$ Å, $\alpha = 113.20(5)$, $\beta = 85.96(5)$, and $\gamma = 99.11(5)°$; (**2**) is monoclinic and crystallizes in space group $P2_1/c$, $Z = 4$ with $a = 15.002(5)$, $b = 10.889(4)$, $c = 8.819(4)$ Å, and $\beta = 105.2(5)°$; (**3**) is triclinic and crystallizes in space group $P\bar{1}$, $Z = 2$, with $a = 16.313(8)$, $b = 8.386(5)$, $c = 6.661(4)$ Å, $\alpha = 85.70(6)$, $\beta = 98.08(6)$, and $\gamma = 100.46(6)°$. Complex (**1**) comprises two $Re(bipy)(CO)_3$ units, linearly bonded by an hydrogen atom. The Re ··· Re distance between the two moieties is 3.49 Å. The structures of (**2**) and (**3**) exhibit the same half octahedron $Re(bipy)(CO)_3$ axially bonded respectively to HCO_2^- and $BH_3(CN)^-$.

The organometallic chemistry of rhenium polypyridyl complexes is scarcely developed[1–5] and the crystal structures of only two of them have recently been reported.[3,4] Most of these complexes present long-lived charge-transfer excited states in fluid solution at room temperature.[2,5] We have recently shown that the photophysical and electrochemical properties of (2,2′-bipyridine)tricarbonylhalogenorhenium(I) complexes are greatly dependent on the ligand substitution by donor or acceptor groups.[5]

In the course of our work on carbon dioxide activation by photochemical and electrochemical means using *fac*-$[Re(bipy)(CO)_3Cl]$ (bipy = 2,2′-bipyridine) as a catalyst, new complexes have been isolated and characterized.[6,7] We report here the *X*-ray crystal structure of two of them as well as the synthesis and the crystal structure of a complex with cyanotrihydroborate co-ordinated to the rhenium centre. Chemical transformations and structural formulae for the new complexes are shown in the Scheme. Our interest in the synthesis of rhenium hydrides arose from the fact that during irradiation of $[Re(bipy)(CO)_3Cl]$ in dimethylformamide (solvent)–triethanolamine (electron donor) under a carbon dioxide atmosphere $[Re(bipy)(CO)_3(HCO_2)]$ (**2**) was formed in small amounts in the absence of an excess of chloride ions. This compound results mainly from CO_2 insertion into a hydridorhenium complex formed in the photochemical reaction.[6–8] During our attempts to synthesize $[Re(bipy)(CO)_3H]$,[8] by reaction of $NaBH_4$ with $[Re(bipy)(CO)_3Cl]$ or $[Re(bipy)(CO)_3(H_2O)]BF_4$ a hydrido complex was isolated, which was found to be the hydrido-bridged species (**1**). When sodium cyanotrihydroborate was used as a hydride source, only displacement of the chloride ion by $BH_3(CN)^-$ was observed and no bridge hydrido compound was formed. These complexes represent the first structural characterization of a bridged hydridorhenium(I) bipyridine species and of a unidentate HCO_2^- or $BH_3(CN)^-$ group co-ordinated to a single rhenium centre.

Experimental

The synthesis and characterization of compounds (**1**) and (**2**) have been reported previously.[7] The three crystal structures were solved and refined using SHELX76[9] programs. The weights were in the form $w = 1/[\sigma(F)^2 + \varepsilon F^2]$, where $\sigma(F)$ is taken from diffractometer counting statistics, F is the observed structure factor, and ε is a refined constant with values 0.0015 (**1**), 0.006 (**2**) and 0.0012 (**3**). Suitable single crystals of complex (**1**) were obtained by slow diffusion of pentane into an acetone solution at low temperature (*ca.* −20 °C) under argon, in the absence of light. A crystal of about 0.4 × 0.3 × 0.05 mm was mounted on a four-circle automatic diffractometer, using Mo-K_α (0.7107 Å) radiation. From 7 862 collected reflections, 6 334 were regarded as observed $[I > 3\sigma(I)]$. The following scan conditions were used: speed 0.04° s^{-1}, width 1°, background 2 × 5 s, and θ range 2—30°.

The cell is triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 18.848(9)$, $b = 10.171(5)$, $c = 8.449(4)$ Å, $\alpha = 113.20(5)$, $\beta = 85.96(5)$, $\gamma = 99.11(5)°$, $U = 1\,392$ Å^3, $D_c = 2.13$ g cm^{-3}, $F(000) = 892$, and $M = 889.3$. Lorentz and polarization corrections were applied. There are two $Re(bipy)(CO)_3$ units per asymmetric unit. The rhenium co-ordinates were found on a Patterson map, and light atoms appeared on successive Fourier difference maps, including three water molecules. At the end of the isotropic refinement ($R = 0.130$), an empirical absorption correction[10] was calculated, which lowered R to 0.052. Anisotropic refinement led to the location of all hydrogen atoms but two belonging to water molecules. The final R value was 0.033 ($R' = 0.037$).

Single crystals of complex (**2**) were obtained by layering an acetonitrile solution of the compound with hexane, at room temperature in air. The structure was studied using a minute

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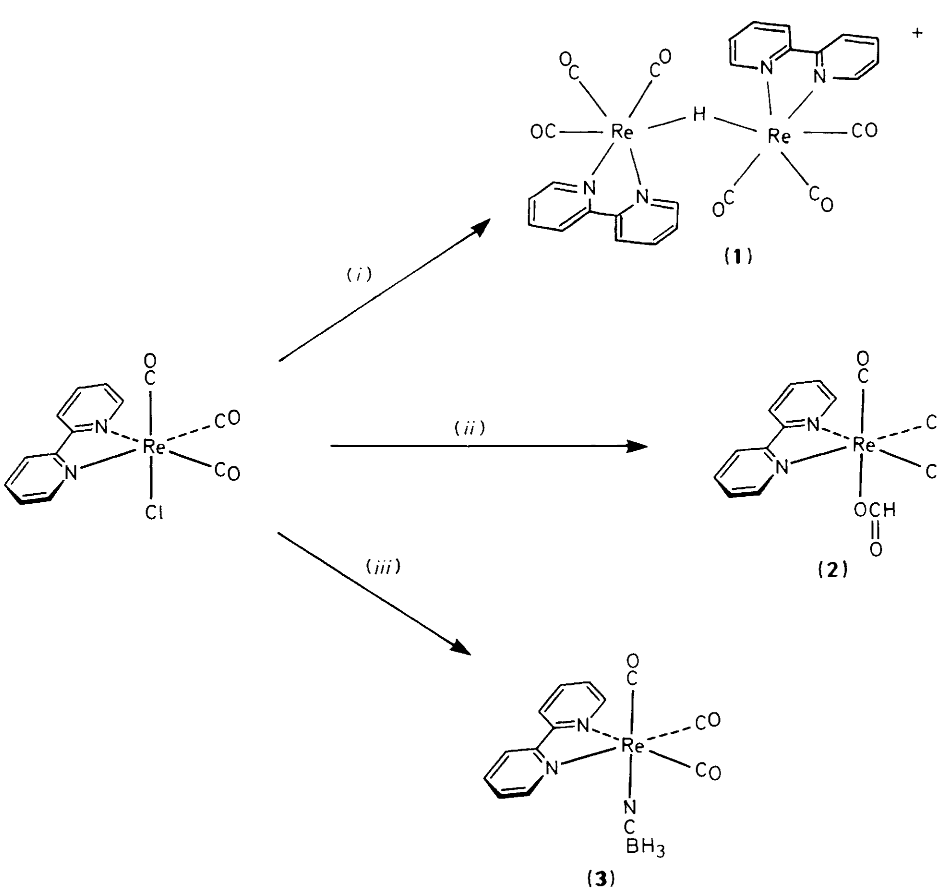
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. (*i*) $NaBH_4$; (*ii*) *h*ν, CO_2, triethanolamine; (*iii*) $Na[BH_3(CN)]$

Table 1. Rhenium co-ordination polyhedra of $[Re_2(bipy)_2(CO)_6(\mu\text{-}H)]Cl$ (distances in Å, angles in °)

Angles around Re(A)

	C(2)	C(3)	N(1A)	N(1A′)
C(1)	90.5	88.0	172.0	98.4
C(2)		88.9	93.5	94.1
C(3)			98.7	172.9
N(1A)				74.7

Angles around Re(B)

	C(2′)	C(3′)	N(1B)	N(1B′)	Re(A)
C(1′)	89.5	89.2	170.7	96.7	90.6
C(2′)		89.9	94.8	96.4	173.8
C(3′)			99.0	171.3	83.9
N(1)				74.6	85.9
N(1B′)					89.7

Bond lengths

	C(1)*	C(2)*	C(3)*	N(1)	N(1′)
Re(A)	1.921(5)	1.938(6)	1.913(8)	2.162(4)	2.171(4)
Re(B)	1.904(5)	1.908(6)	1.920(7)	2.165(4)	2.160(4)

* C(1′), C(2′), and C(3′) for Re(B).

fragment from a twinned crystal. Crystal data are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 15.002(5)$, $b = 10.889(4)$, $c = 8.819(4)$ Å, $\beta = 105.2(5)°$, $U = 1\,392$ Å^3, $D_c = 2.25$ g cm^{-3}, $F(000) = 888$, and $M = 471.4$. The data were collected as for complex (**1**). From 4 490 measured reflections only 738 were significant at the $2\sigma(I)$ level.

The structure was solved by the heavy-atom method and refined to R 0.078, with anisotropic thermal parameters for the rhenium atom only, and using rigid blocks for the pyridine rings, in order to decrease the number of variable parameters, to take into account the lack of data. Hydrogen atoms were introduced at their calculated positions.

Complex (**3**) was typically prepared from $[Re(bipy)(CO)_3Cl]$ (100 mg, 0.22 mmol) dissolved in 30 cm^3 degassed ethanol–water (4:1), and $Na[BH_3(CN)]$ (70 mg, 1.11 mmol, 5 equiv.) under reflux and an inert atmosphere. After 10 h most of the solvent was evaporated *in vacuo*. The product was extracted into dichloromethane (3 × 50 cm^3). The organic phase was washed three times with water (10 cm^3), dried over magnesium sulphate, and evaporated to dryness under vacuum. Chromatography on an alumina column using ethyl acetate–methanol (4:1) gave 65 mg (64%) of complex (**3**) ($R_F = 0.7$) (Found: C, 38.60; H, 3.60; N, 7.55. $C_{18}H_{21}BN_3O_5Re$ requires C, 38.85; H, 3.80; N, 7.55%). N.m.r: ^1H (200.1 MHz, CD_2Cl_2): 9.03 [2 H, d, H–C(6,6′)], 8.46 [2 H, d, H–C(3,3′)], 8.26 [2 H, td, H–C(4,4′)], 7.69 ([2 H, td, H–C(5,5′)], and 0.25 [3 H, large q, $BH_3(CN)$]; ^{13}C (100.6 MHz, CD_2Cl_2) 196.4 (CO), 199.6 (CO), 156.5, 154.3, 140.8, 128.6, and 124.3 p.p.m. I.r. (CH_2Cl_2): 2 200 [$BH_3(CN)$], 2 030 and 1 928 cm^{-1} (carbonyls). U.v. (CH_2Cl_2): $\lambda_{max.}$ 360 nm ($\varepsilon = 4\,400$ dm^3 mol^{-1} cm^{-1}).

Single crystals of the tetrahydrofuran-soluble compound $[Re(bipy)(CO)_3\{BH_3(CN)\}]$ were prepared by vapour diffusion of pentane at room temperature under argon. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 16.313(8)$, $b = 8.386(5)$, $c = 6.661(4)$ Å, $\alpha = 85.70(6)$, $\beta = 98.08(6)$, $\gamma = 100.46(6)°$ $U = 886$ Å^3, $D_c = 2.08$ g cm^{-3}, $F(000) = 540$, and $M = 466.3$. The data were collected as for complex (**1**). Of 5 970 measured reflections, 3 841 were used [$I > 3\sigma(I)$].

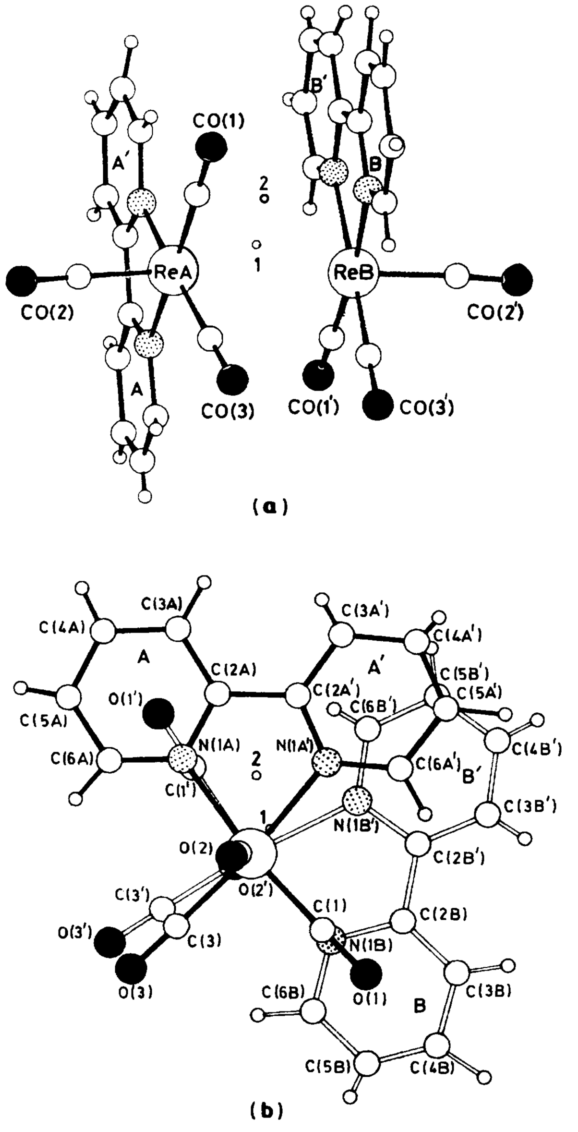


Figure 1. Crystal structure of the hydrido-bridged complex [$Re_2(bipy)_2(CO)_6(\mu$-H)]Cl (**1**): (*a*) perpendicular to the Re–μ-H–Re plane; (*b*) along the Re–Re axis

The structure was solved by the heavy-atom method, and refined by full-matrix least squares. A water molecule and also a very disordered tetrahydrofuran molecule were located. The latter was submitted to constraints in the first stages of the refinement, then released. The final *R* value was 0.081.

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

Results and Discussion

The hydrido-bridged complex [$Re_2(bipy)_2(CO)_6(\mu$-H)]Cl is represented in Figure 1(*a*) and (*b*). Each rhenium has four equatorial bonds, two with carbonyl groups, and two with the nitrogens of the bipyridine. Those four bonds are coplanar (0.02 Å), and each rhenium is situated in this plane (0.04 Å). The axial bonds Re–C(2), Re–C(2′) are perpendicular to it.

The two square pyramids have their bases facing each other and rotated by nearly 90°, the equatorial bonds being almost eclipsed. This places an oxygen of a carbonyl in the hollow of the superimposed aromatic ring, thus achieving a tight internal packing (see Figure 2).

The dimensions of the co-ordination octahedra are given in Table 1, atomic co-ordinates in Table 2. All Re–N distances are equal (2.16 Å). There are no real differences between the equatorial Re–CO bonds [average: 1.915, root-mean-square (r.m.s.) deviation 0.007 Å], but the two axial bonds differ

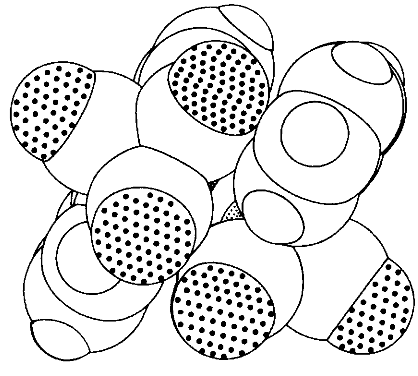


Figure 2. Space-filling representation of complex (**1**)

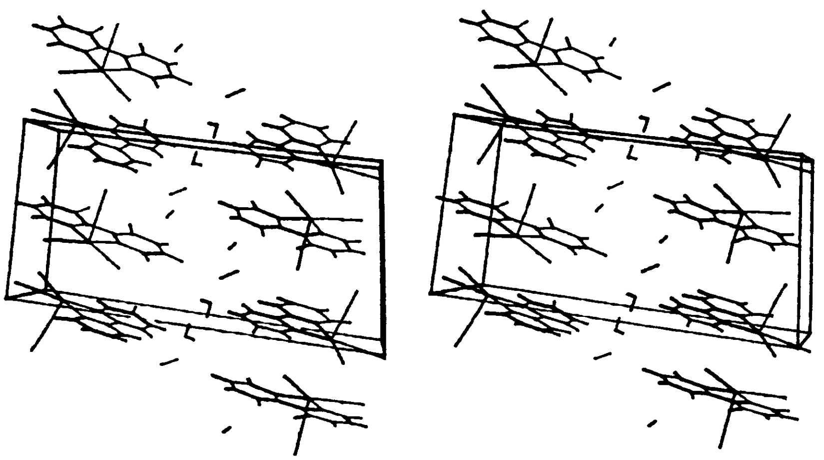


Figure 3. Crystal packing of complex (**1**)

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses (W = water, TH = tetrahydrofuran)

Atom	*x*	*y*	*z*
Complex (**1**)			
Re(A)	7 984(1)	6 444(1)	1 846(1)
N(1A)	8 285(2)	5 619(4)	−850(5)
C(2A)	7 757(3)	5 391(5)	−1 989(6)
C(3A)	7 896(4)	4 856(6)	−3 776(6)
C(4A)	8 580(4)	4 589(7)	−4 376(8)
C(5A)	9 109(4)	4 823(7)	−3 208(9)
C(6A)	8 948(3)	5 342(7)	−1 453(8)
N(1A′)	7 017(2)	6 259(4)	473(5)
C(2A′)	7 051(3)	5 735(5)	−1 255(6)
C(3A′)	6 460(4)	5 555(8)	−2 228(9)
C(4A′)	5 817(4)	5 935(10)	−1 413(11)
C(5A′)	5 781(3)	6 469(7)	321(9)
C(6A′)	6 388(3)	6 625(6)	1 248(8)
C(1)	7 622(3)	7 294(6)	4 153(6)
O(1)	7 393(3)	7 803(5)	5 517(5)
C(2)	7 751(3)	4 534(5)	1 891(7)
O(2)	7 628(3)	3 449(5)	1 985(6)
C(3)	8 899(4)	6 613(7)	2 812(9)
O(3)	9 448(3)	6 703(6)	3 372(8)
Re(B)	8 595(1)	9 765(1)	1 563(1)
N(1B)	8 193(2)	10 721(4)	4 170(5)
C(2B)	7 497(3)	10 941(5)	4 370(6)
C(3B)	7 187(4)	11 480(6)	5 990(7)
C(4B)	7 602(4)	11 806(6)	7 443(7)
C(5B)	8 278(5)	11 574(8)	7 233(8)
C(6B)	8 579(3)	11 024(6)	5 604(7)
N(1B′)	7 501(2)	10 026(4)	1 299(5)
C(2B′)	7 111(3)	10 579(5)	2 776(6)
C(3B′)	6 401(3)	10 750(7)	2 723(9)
C(4B′)	6 068(4)	10 343(8)	1 181(11)
C(5B′)	6 447(4)	9 756(8)	−312(10)
C(6B′)	7 166(4)	9 619(7)	−198(8)
C(1′)	8 791(3)	8 822(6)	−832(7)
O(1′)	8 902(3)	8 245(5)	−2 312(6)
C(2′)	9 032(3)	11 558(6)	1 467(7)
O(2′)	9 310(3)	12 638(5)	1 409(6)
C(3′)	9 515(3)	9 427(6)	2 056(8)
O(3′)	10 060(3)	9 219(6)	2 365(8)
Cl	4 696(1)	2 350(2)	4 693(2)
W(1)	3 736(3)	6 826(6)	78(8)
W(2)	5 925(3)	4 480(8)	3 632(7)
W(3)	4 558(4)	8 852(8)	2 919(9)
Complex (**2**)			
Re	2 073(2)	10 560(2)	1 581(2)
N(1)	3 026(18)	9 741(15)	3 652(24)
C(2)	3 088(18)	8 465(15)	3 626(24)
C(3)	3 723(18)	7 852(15)	4 826(24)
C(4)	4 296(18)	8 516(15)	6 053(24)
C(5)	4 234(18)	9 793(15)	6 079(24)
C(6)	3 599(18)	10 405(15)	4 878(24)
N(1′)	1 816(15)	8 617(20)	1 287(22)
C(2′)	2 419(15)	7 867(20)	2 369(22)
C(3′)	2 305(15)	6 596(20)	2 294(22)
C(4′)	1 588(15)	6 075(20)	1 138(22)
C(5′)	985(15)	6 825(20)	56(22)
C(6′)	1 099(15)	8 096(20)	130(22)
O	3 227(23)	10 079(25)	608(30)
C	3 812(30)	10 689(38)	368(40)
O′	4 025(31)	11 624(37)	954(43)
CCO(1)	2 496(36)	12 103(40)	1 894(47)
OCO(1)	2 586(25)	13 290(31)	2 217(33)
CCO(2)	1 269(32)	10 985(32)	−261(44)
OCO(2)	713(24)	11 277(27)	−1 471(33)
CCO(3)	1 136(38)	10 727(49)	2 570(52)
OCO(3)	531(25)	10 957(28)	3 159(35)

Table 2 (*continued*)

Atom	*x*	*y*	*z*
Complex (**3**)			
Re	2 582(0.4)	4 379(0.6)	1 618(0.8)
N(1)	3 369(7)	3 223(14)	3 605(16)
C(2)	3 510(9)	1 840(16)	3 023(22)
C(3)	3 949(9)	968(16)	4 308(23)
C(4)	4 337(11)	1 489(22)	6 139(27)
C(5)	4 245(12)	3 053(22)	6 680(30)
C(6)	3 750(10)	3 827(18)	5 364(21)
N(1′)	2 656(7)	2 182(14)	148(15)
C(2′)	3 129(11)	1 281(17)	1 083(20)
C(3′)	3 255(13)	−12(19)	145(24)
C(4′)	2 819(17)	−469(22)	−1 753(32)
C(5′)	2 367(13)	412(25)	−2 628(30)
C(6′)	2 300(13)	1 777(16)	−1 783(19)
CCO(1)	1 753(11)	3 319(24)	2 959(27)
OCO(1)	1 287(11)	2 809(24)	3 706(29)
CCO(2)	1 911(12)	5 229(22)	−470(27)
OCO(2)	1 528(10)	5 765(20)	−1 833(25)
CCO(3)	2 651(9)	6 224(18)	3 147(21)
OCO(3)	2 671(9)	7 283(17)	4 187(16)
N	3 502(9)	5 565(15)	234(20)
C	3 999(9)	6 318(16)	−599(20)
B	4 603(11)	7 292(21)	−1 688(29)
W	1 259(7)	−1 431(18)	−2 244(19)
O(1TH)	1 105(42)	8 650(73)	3 137(105)
C(2TH)	985(34)	8 458(58)	1 080(86)
C(3TH)	219(42)	7 339(76)	586(96)
C(4TH)	533(78)	7 784(121)	3 972(140)
C(5TH)	0(42)	7 295(75)	2 465(116)

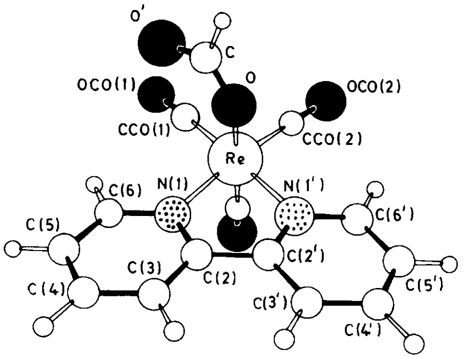


Figure 4. Crystal structure of the formato complex *fac*-[Re(bipy)(CO)$_3$(HCO$_2$)] (**2**)

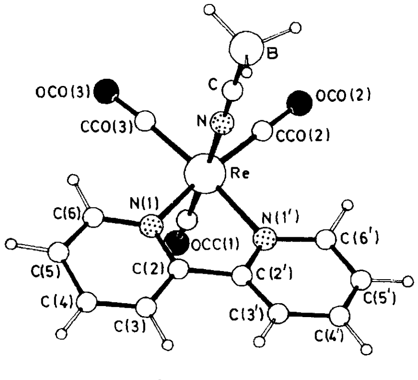


Figure 5. Crystal structure of the cyanotrihydroborate complex *fac*-[Re(bipy)(CO)$_3${BH$_3$(CN)}] (**3**)

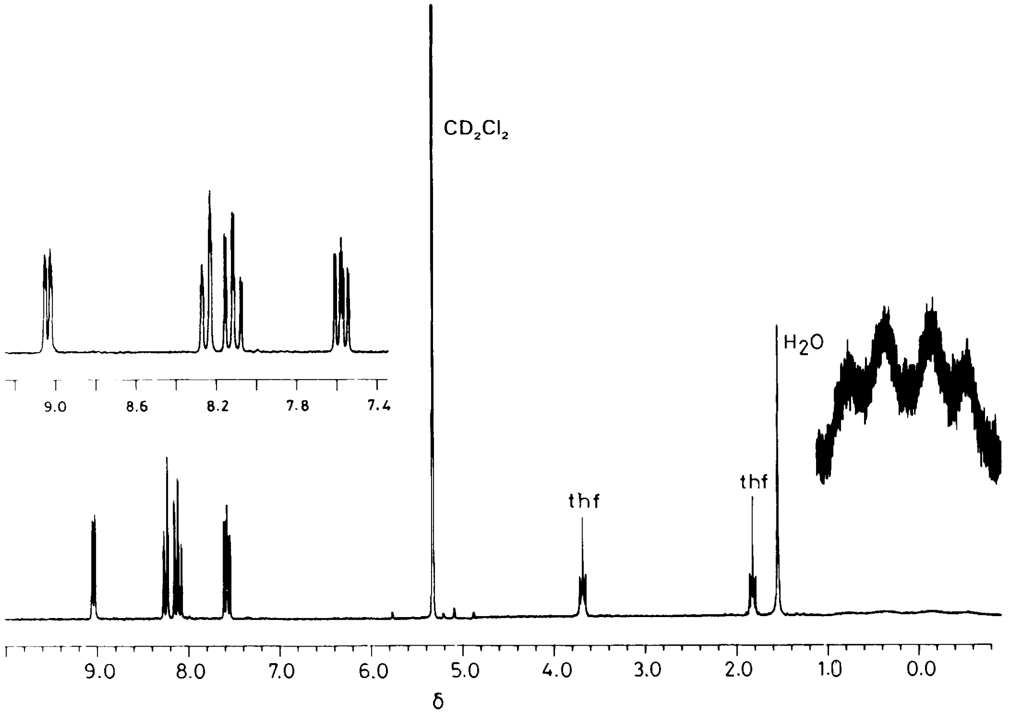


Figure 6. 400-MHz ^{1}H n.m.r. spectrum of a single crystal of complex (**3**) dissolved in CD_2Cl_2. From left to right, the multiplets may be assigned to protons at positions 6,6′ (9.03), 3,3′ (8.46), 4,4′ (8.26), 5,5′ (7.69), and $BH_3(CN)$ (0.25); the tetrahydrofuran peaks (thf) arise from the molecule of solvent contained in the structure (see text)

slightly (1.904 and 1.938 Å). The axial line O(2)–C(2)–Re(A)–Re(B)–C(2′)–O(2′) is slightly bent: 12° between the directions of the axial bonds.

The two bipyridine planes are parallel (2°). However, whereas the two equatorial carbonyls of Re(A) are strictly in the aromatic plane, the plane formed by the equatorial carbonyls bonded to Re(B) makes a dihedral angle of 9° with the bipyridine plane, and is inclined towards Re(A). The following short distances are observed: N(1A) ••• C(1′) 3.23 (superimposed atoms), C(3) ••• C(3′) 3.20, and O(3) ••• O(3′) 3.04 Å. No deformation occurs with C(1) and O(1) (3.15 Å to bipyridine B). There is one chlorine anion for the two Re units.

We looked for the missing (bridging) hydrogen on the Fourier difference map. The highest residues on the final electron-density map are of the order of 1 e Å^{-3}. Of the ten first spurious peaks, eight are in a shell of radius 1 Å from each rhenium and were discarded. The two other peaks are exactly halfway between the rheniums:

	Re(A)	Re(B)	Re(A)–peak–Re(B)
Peak 1	1.86 Å	1.86 Å	144°
Peak 2	2.26 Å	2.26 Å	100°

Although the accuracy is such that one of these peaks could not be unambiguously attributed to hydrogen, it is reasonable to place a hydrogen atom in a bridging position: this would complete the 18-electron shell around each rhenium, the entire complex behaving as a cation.

The distance between the rheniums (3.49 Å) is 0.7 Å longer than the sum of the metallic radii, and does not correspond to a metal–metal bond: the longest Re ••• Re distances observed, to our knowledge, are 3.26 Å in $[Re_3(CO)_{10}(\mu\text{-}O_2CH)H_3]^-$ [11] and 3.39 Å in $[Re_2Mn(CO)_{14}H]$.[12] These long distances are similarly attributed to a bridging hydrogen. The crystal packing (Figure 3) shows the presence of three water molecules involved in an hydrogen-bonding network with the chlorine anions.

The monomeric complex *fac*-[Re(bipy)(CO)$_3$(HCO$_2$)] (Figure 4) shows an eclipsed orientation of the axial formate plane with respect to one of the equatorial carbonyl groups. Unfortunately the lack of precision on bond lengths and angles due to a lack of experimental diffraction data does not allow a more detailed analysis of the geometrical parameters. One may note that the i.r. and ^{13}C n.m.r. data for the CO groups in complex (**2**)[7] are similar to those of *fac*-[Re(bipy)(CO)$_3$Cl].[13] In [Re(bipy)(CO)$_3$(PO$_2$F$_2$)] each P–O bond was also found to be nearly eclipsed with one of the equatorial carbonyl functions.[3] The monomeric cyanotrihydroborate complex (**3**) is shown in Figure 5. The ^{1}H n.m.r. spectrum (Figure 6) shows that the hydride signal of $BH_3(CN)$ is broad and that the H–B coupling constant is smaller when $BH_3(CN)$ is co-ordinated to the rhenium [*J*(H–B) = 83.6 Hz] than in Na[BH$_3$(CN)] [*J*(H–B) = 88.5 Hz]. The bond lengths (Re–N 1.95, N–C 1.12, and C–B 1.41 Å) are somewhat shorter than those found in other complexes where $BH_3(CN)$ is bound to Cu^{II} (Cu–N 1.98, N–C 1.14, and C–B 1.55 Å).[14]

In conclusion, starting from *fac*-[Re(bipy)(CO)$_3$Cl] it has been possible to prepare a bridged hydridorhenium(I) dimer, a formate, and a cyanotrihydroborate unit co-ordinated to a single rhenium centre. All three crystal structures consist of the same half octahedron [*fac*-Re(bipy)(CO)$_3$] bonded respectively to HRe(bipy)(CO$_3$), HCO_2^- and $BH_3(CN)^-$.

Acknowledgements

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References

1 N. M. Boog and H. D. Goesz, in 'Comprehensive Organometallic Chemistry,' Pergamon, Oxford, 1982, vol. 4, p. 161.

2 G. L. Geoffroy and M. S. Wrighton, in 'Organometallic Photochemistry,' Academic Press, New York, 1979, p. 89; J. V. Caspar, B. P. Sullivan, and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 2104.

3 E. Horn and M. R. Snow, *Aust. J. Chem.*, 1980, **33**, 2369.

4 M. Stebler, A. Gutiérrez, A. Ludi, and H. B. Bürgi, *Inorg. Chem.*, 1987, **26**, 1449.

5 A. Juris, S. Campagna, I. Bidd, J-M. Lehn, and R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007.

6 J. Hawecker, J-M. Lehn, and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536; 1984, 328.

7 J. Hawecker, J-M. Lehn, and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990.

8 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1984, 1224; *Organometallics*, 1986, **5**, 1500.

9 G. M. Sheldrick, SHELX76, Program for crystal structure determination, University of Cambridge, 1976.

10 N. Walter and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

11 T. Beringhelli, G. Ciani, G. D'Alfonso, A. Sironi, and M. Freni, *J. Organomet. Chem.*, 1982, **233**, C46.

12 H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, 1967, **89**, 2775.

13 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501; F. Zingales, M. Graziani, F. Foraone, and U. Belluco, *Inorg. Chim. Acta*, 1967, **1**, 172.

14 B. G. Segal and S. J. Lippard, *Inorg. Chem.*, 1974, **13**, 822.

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