Neutron Diffraction Study of [K(18-crown-6)] [$(PPh_3)_2ReH_6Cr(CO)_3$], a Bimetallic Donor-Acceptor Complex☆

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Received February 2, 1998

Keywords: Neutron diffraction / Donor-acceptor complex / Bridging hydride ligand / Rhenium / Chromium

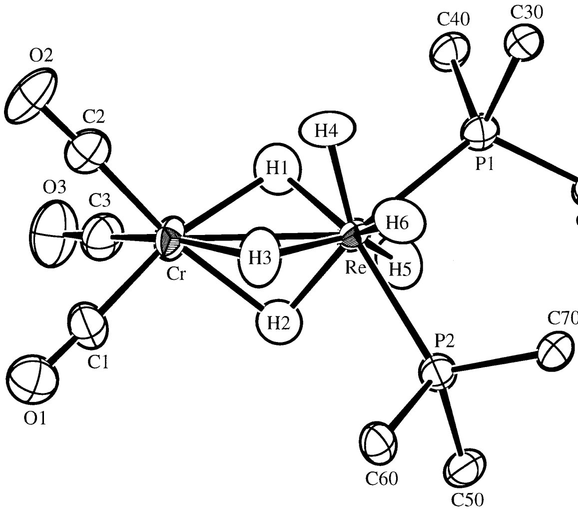
A neutron diffraction analysis was carried out at 120 K on a single crystal of [K(18-crown-6)][$(PPh_3)_2ReH_6Cr(CO)_3$]·THF in order to locate the hydride ligands. Three of the hydrides are bound terminally to the Re atom while the other three bridge the Re–Cr bond; the bridging hydrides are closer to the Re atom. This compound can be thought of as a donor–acceptor complex, with $[(PPh_3)_2ReH_6]^-$ acting as the donor to the $Cr(CO)_3$ fragment. Average distances and angles: Re–Cr = 2.58(1), Re–H(br) = 1.75(1), Cr–H(br) = 1.92(2), Re–H(t) = 1.69(1) Å; Re–H–Cr = 89.1(7)°. Final agreement factors: $R(F)$ = 6.4% for 3443 reflections with $I > 2\sigma(I)$, and $R(F)$ = 8.3% for all data (4195 reflections).

The concept of a transition metal hydride complex functioning as a ligand has been attracting an increasing amount of attention.[1][2][3][4][5][6][7] In recent years, several cases have been documented in which a metal hydride acts as a donor to a second (otherwise electron-deficient) metal atom. The donor-acceptor interaction in the resulting compound takes place through the bridging hydride ligands, much as in a borohydride complex.[8] In this communication we report the neutron structure determination of one such compound, the $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ anion, and provide the first accurate characterization of a Re−H−Cr bridging system.

[K(18-crown-6)][$(PPh_3)_2ReH_6Cr(CO)_3$] is made by reaction of [K(18-crown-6)] [$(PPh_3)_2ReH_6$] with $(CH_3CN)_3Cr(CO)_3$ in THF.[1] Crystals were obtained by the addition of diethyl ether to a THF solution of the title compound. Neutron diffraction data were collected at the Institut Laue-Langevin at 120 K on a sample with volume 4 mm³, and the structure was refined to a final agreement factor of $R(F)$ = 6.4% (Experimental Section).

The structure of the $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ unit is shown in Figure 1, and selected distances and angles listed in Table 1. Three of the H ligands bridge the Re−Cr bond and three are terminal on Re, as predicted.[1] The bridging H atoms are closer to the Re atom [average Re−H = 1.75(1) Å, average Cr−H = 1.92(2) Å], despite the smaller size[9] of chromium. This suggests that the complex as a whole is best viewed as a donor-acceptor complex in which an 18-electron $[(PPh_3)_2ReH_6]^-$ moiety serves as a 6−electron donor, through the three bridging H atoms, to a 12-electron $Cr(CO)_3$ fragment. The average Re−H−Cr angle is 89.1(7)°, comparable to other compounds having M−(μ−H)$_3$−M bridges.[10] The Re−Cr bond length, 2.58(1) Å, is much shorter than the single-bonded Re−Cr distance of 3.05 Å,[11] suggesting some level of multiple bonding. Indeed, $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ as a whole is isoelectronic with $[Re_2H_9(triphos)]^-$, a compound considered to have a formal triple bond.[3]

Figure 1. A plot of the core of the $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ anion, with all but the *ipso* carbons of the phenyl groups removed for clarity



As anticipated earlier,[1] the eight ligands around the Re atom (not counting the Re−Cr bond) define the familiar dodecahedral arrangement[12] of two interpenetrating trapezoids. Figure 2 shows this clearly: atoms H1, H4, H6, and P2 are virtually co-planar (within ±0.01 Å), and define one trapezoid, which is essentially perpendicular to the other

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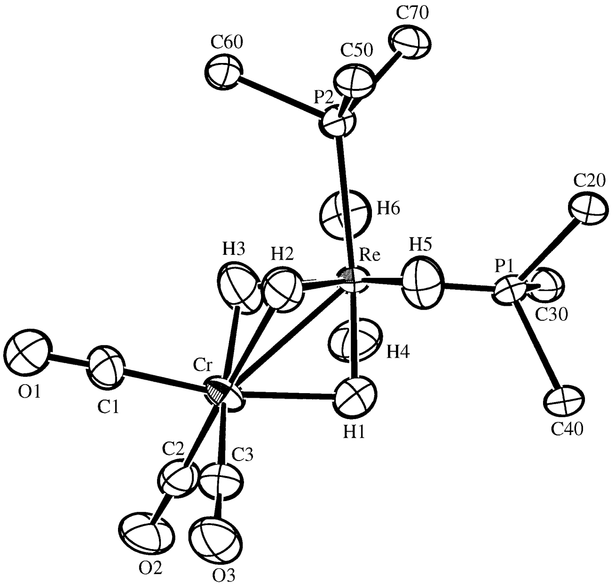
Table 1. Selected distances [Å] and angles [°]

Re−Cr	2.58(1)		
Re−P(1)	2.39(1)	Re−P(2)	2.38(1)
Re−H(1)	1.75(1)	Re−H(4)	1.69(1)
Re−H(2)	1.76(1)	Re−H(5)	1.70(1)
Re−H(3)	1.74(1)	Re−H(6)	1.69(1)
Cr−H(1)	1.94(2)	Cr−C(1)	1.81(1)
Cr−H(2)	1.95(2)	Cr−C(2)	1.80(1)
Cr−H(3)	1.87(2)	Cr−C(3)	1.82(1)
P(1)−Re−H(1)	88.0(5)	P(2)−Re−H(1)	156.4(5)
P(1)−Re−H(2)	139.3(5)	P(2)−Re−H(2)	81.9(5)
P(1)−Re−H(3)	148.1(5)	P(2)−Re−H(3)	92.3(5)
P(1)−Re−H(4)	75.2(5)	P(2)−Re−H(4)	133.9(5)
P(1)−Re−H(5)	66.6(5)	P(2)−Re−H(5)	85.3(5)
P(1)−Re−H(6)	84.3(5)	P(2)−Re−H(6)	67.3(5)
H(1)−Re−H(2)	76.9(6)	H(1)−Re−H(3)	90.3(6)
H(1)−Re−H(4)	69.2(6)	H(1)−Re−H(5)	78.8(6)
H(1)−Re−H(6)	135.7(7)	H(2)−Re−H(3)	70.5(6)
H(2)−Re−H(4)	130.4(6)	H(2)−Re−H(5)	73.5(6)
H(2)−Re−H(6)	132.1(6)	H(3)−Re−H(4)	74.5(6)
H(3)−Re−H(5)	143.8(7)	H(3)−Re−H(6)	74.9(6)
H(4)−Re−H(5)	130.5(7)	H(4)−Re−H(6)	66.6(6)
H(5)−Re−H(6)	135.2(7)		
Cr−Re−H(4)	81.2(5)	Cr−Re−P(1)	136.1(3)
Cr−Re−H(5)	105.2(5)	Cr−Re−P(2)	121.1(4)
Cr−Re−H(6)	119.2(5)	P(1)−Re−P(2)	101.8(3)
H(1)−Cr−H(2)	68.2(6)	C(1)−Cr−H(1)	167.9(8)
H(2)−Cr−H(3)	63.6(6)	C(2)−Cr−H(2)	168.0(8)
H(1)−Cr−H(3)	80.9(7)	C(3)−Cr−H(3)	168.3(8)
C(1)−Cr−Re	127.4(6)	Re−H(1)−Cr	88.4(6)
C(2)−Cr−Re	125.9(6)	Re−H(2)−Cr	88.0(6)
C(3)−Cr−Re	128.9(6)	Re−H(3)−Cr	91.0(7)

Figure 2. An alternative view of the $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ core, plotted in such a way as to show the coordination around the Re atom, which consists of two intepenetrating trapezoids. The coplanar atoms H3, H2, H5, and P1 define one trapezoid, which is approximately perpendicular (87°) to the other trapezoid, defined by the coplanar atoms H1, H4, H6, and P2. Because of this arrangement, the three H−Re−H angles are decidedly unequal to each other, as are the three H−Cr−H angles



trapezoid, defined by atoms H3, H2, H5, and P1 (co-planar within ±0.05 Å). The Re atom is slightly out of plane of both trapezoids. Because of the unsymmetrical positioning of the Re−Cr bond relative to these two interpenetrating trapezoids (one trapezoid contains two bridging H ligands while the other one has only one bridging hydride), the Cr−Re−P angles are unequal [Cr−Re−P1 = 136.1(4), Cr−Re−P2 = 121.1(4)°]. The closest H···H non-bonding contacts are those along the "sides" of the trapezoids (Figure 2): H4···H6 = 1.85, H1···H4 = 1.96, H2···H3 = 2.02, H2···H5 = 2.07 Å.

The average terminal Re−H distance in the title compound [1.69(1) Å] is, as expected,[3][13] shorter than the average bridging Re−H distance [1.75(1) Å]. The former is comparable to terminal Re−H distances found from other neutron structure determinations (range 1.66 to 1.69 Å),[10] but the latter is unusually short (standard Re−H bridging bond lengths range from 1.81 to 1.88 Å[10]). This suggests that the Re−H bridge in $[(PPh_3)_2ReH_6Cr(CO)_3]^-$ is stronger than a normal bridge (i.e., is somewhat more "terminal" in character).

The Cr atom has the expected distorted octahedral geometry, with C−Cr−H (*trans*) angles that have a mean value of 168.1(8)°. The average Cr−H bond length [1.92(2) Å] is much longer than normal bridging Cr−H distances [range: 1.72−1.73 Å],[14] suggesting a weaker-than-usual chromium-hydrogen interaction.

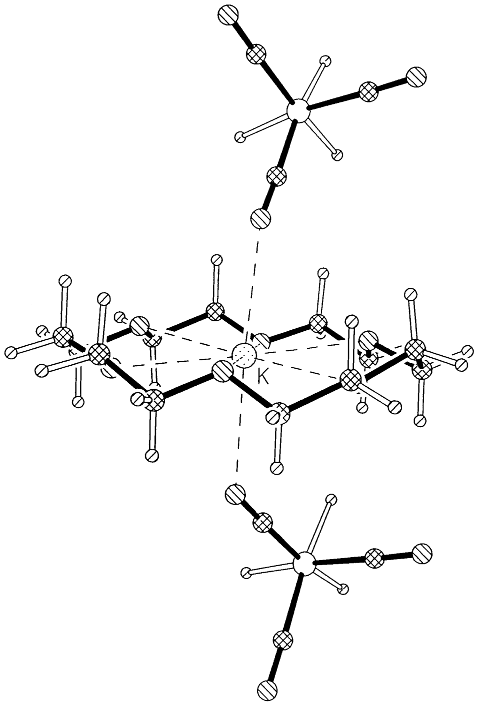
Curiously, the H−Cr−H angles show an unequal distribution [63.6(6), 68.2(6), 80.9(7)°] as do the H−Re−H angles [70.5(6), 76.9(6), 90.3(7)°], presumably because of the steric requirement for maintaining a dodecahedral arrangement of ligands around rhenium.

The K^+ coordination sphere is quite interesting, being made up of the 18-crown-6 ligand and two CO oxygens from separate $Cr(CO)_3$ fragments. This approximately D_{6h}, 8-fold coordination is shown in Figure 3. The THF solvate molecule, which does not bind to the potassium ion and has no other strong interactions, is disordered and was refined as a rigid body in two orientations.

The present structure determination represents the first time that a Re−H−Cr bridging system has been analyzed by neutron diffraction. An earlier X-ray analysis[15] on the single-hydride-bridged complex $(OC)_5Re(H)Cr(CO)_5$ revealed a Re−Cr distance of 3.435(1) Å, but did not locate the bridging H atom. It was originally proposed that the Re−H−Cr bridge in that compound was linear,[15] but that suggestion was made before it became generally accepted that 3-center/2-electron M−H−M bridge bonds are inherently bent.[7][14][16]

Only a few metal hydride complexes of the donor-acceptor type have been accurately analyzed by neutron diffraction. Earlier examples include $[Re_2H_9(triphos)]^-$ {in which $[ReH_9]^{2-}$ is formally a ligand to a $[Re(triphos)]^+$ moiety},[3] $[Pt_2H_3(dppe)_2]^+$ {a complex between $PtH_2(dppe)$ and $[PtH(dppe)]^+$},[4] $[PtIrH_4(PEt_3)_4]^+$ {a complex between $PtH_2(PEt_3)_2$ and $[IrH_2(PEt_3)_2]^+$},[5] and

Figure 3. The coordination around the K^+ ion, which is surrounded by six oxygen atoms from the 18-crown-6 ligand and two carbonyl oxygen atoms in an approximately D_{6h} arrangement. The two axial ligands are the O2 and O3 atoms of the $H_3Cr(CO)_3$ portions of two neighboring anions



$[(PEt_3)_2(C_6Cl_5)PtHAg(H_2O)]^+$, in which a Pt−H bond is a donor to a Ag^+ ion.[6] Also worthy of mention are two complexes in which $[Na(18\text{-crown-}6)]^+$ and $[K(18\text{-crown-}6)]^+$ act as acceptors from a $[WH_5(PMe_3)_3]^-$ fragment.[17] In most cases {except $[Re_2H_9(\text{triphos})]^-$},[3] the hydride ligands are unsymmetrically bridging in such a way as to indicate that they are held much more tightly to the donor atom than the acceptor atom. The structure of the title compound is consistent with this general trend: the short/long pattern of distances in the Re−H−Cr linkage is certainly suggestive of a higher bond order for the Re−H portion than the H−Cr portion of the bridge.

This research was supported by the *National Science Foundation* and the *American Chemical Society* (Petroleum Research Fund).

Experimental Section

The neutron diffraction data set was collected at the Institut Laue-Langevin, Grenoble, France, on the thermal-beam instrument D19, which is equipped with a 4° × 64° position-sensitive detector.[18] A platelike single crystal of dimensions 1.2 × 1.6 × 2.0 mm, volume 4 mm^3, was sealed in epoxy on an Al pin and placed in a Displex cryorefrigerator.[19] It was then indexed and cooled at 2 degrees per minute while the strong (0, 0, 4) reflection was being monitored. Below 117 K the mosaic spread increased and at 95 K the peak was much broader and weaker, so the temperature was raised to 120 K where the mosaic spread was acceptable and the peak intensity restored. Data were initially collected at a neutron wavelength of 1.3139 Å, but this was changed to 1.5394 Å to increase the intensity of the reflections. Bragg intensities were integrated in three dimensions using the ILL program RETREAT.[20] The two sets of intensities were then scaled and merged, and corrected for attenuation by the cylindrical heat shields, and for absorption effects ($\mu = 2.31$ cm^{-1} at 1.3139 Å; 2.55 cm^{-1} at 1.5394 Å) using the program D19ABS, based on the ILL version of the CCSL system.[21] Refinement was begun using the positions of the non-hydrogen atoms obtained from the x-ray structure determination;[1] the positions of the organic hydrogen atoms were calculated and subjected to several cycles of least-squares refinement. The hydride ligands were readily found in a difference Fourier map. All atoms except those of the disordered THF molecule were refined anisotropically[22a] to yield final agreement factors of $R(F) = 6.4\%$ for 3443 reflections with $I > 2\sigma(I)$, and $R(F) =$ 8.3% for all data (4195 reflections). The neutron scattering lengths used in the refinement were those tabulated by Sears.[22b]

Supplementary Material: A summary of the results of the neutron diffraction study, with final atomic positions and a complete listing of distances and angles in the title compound, have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC−100889. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk; fax: +44(0)1223/336-033).

☆ Dedicated to the 70th birthday of Prof. *Heinrich Nöth.*

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