Crystal structure of *cis*-bis(triphenylphosphine)-*fac*-(tricarbonyl)-rhenium(I) bromide, $\text{Re}(\text{CO})_3(\text{C}_{18}\text{H}_{15}\text{P})_2\text{Br}$

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Abstract

$\text{C}_{39}\text{H}_{30}\text{BrO}_3\text{P}_2\text{Re}$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.43(6)$ Å, $b = 38.6(3)$ Å, $c = 9.98(8)$ Å, $\beta = 108.2^\circ$, $V = 3451.0$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.057$, $wR_{\text{obs}}(F) = 0.065$, $T = 293$ K.

Source of material

The rhenium carbonyl complex was prepared by refluxing a petroleum ether (373 K – 393 K) solution containing $\text{Re}(\text{CO})_5\text{Br}$ [1] and a 10% molar excess of two molar equivalents of triphenylphosphine (LN) for two hours, in a similar way as reported earlier [2]. Transparent yellow-brown crystals of the product were obtained by slow recrystallization from dichloromethane at room temperature.

Discussion

Manganese and rhenium pentacarbonyl bromide complexes readily undergo substitution reactions with ligands containing nitrogen or phosphorus atoms to give stable products suitable as precursors for the synthesis of a variety of organometallic compounds [3–5]. This work is part of a carbonyl-ligand exchange study [2, 4–7] which correlates the geometric structure with the carbonyl stretching patterns [8] of complexes of the type, $[\text{M}(\text{CO})_n(\text{LN})_m(\text{X})]$, where M = manganese or rhenium, LN = nitrogen or phosphorus containing ligands, X = Br, ClO_4 , F, OH or PO_2F_2 , $n = 3$ or 5, and $m = 0$ or 1. More specifically, for such complexes, where LN = 2PPh_3 or $2\text{P}(\text{OPh})_3$, the respective *cis*- or *trans*-isomers and *fac*- or *mer*-geometric isomers are possible.

The X-ray analysis reported here characterizes the stereochemistry of the three carbonyl ligands of the $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Br}]$ complex to be in a *fac*-arrangement. The ORTEP plot (30% probability ellipsoids) shows the rhenium atom in a distorted octahedral geometry due to the PPh_3 groups in a *cis*-geometry. The $\text{P}(1)\text{—Re}(1)\text{—P}(2)$ bond angle of $103.3(4)^\circ$ reflects the steric repulsion between the two mono-dentate phosphorus ligands, and the average P—Re bond distance is equal to $2.547(6)$ Å. The bromine atom is located in an axial position with $d(\text{Re1—Br1}) = 2.605(1)$ Å, and the average C—Re bond distance is $1.94(1)$ Å. The other bond lengths and angles are normal.

Table 1. Data collection and handling.

Crystal:	yellow-brown, prismatic, size $0.150 \times 0.150 \times 0.250$ mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ :	48.04 cm^{-1}
Diffractionmeter, scan mode:	Rigaku AFC7R, ω
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	10759, 10466
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7817
$N(\text{param})_{\text{refined}}$:	412
Programs:	SIR92 [9], teXsan [10], ORTEP-II [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.4282	0.1496	1.1398	0.086
H(2)	4e	0.5853	0.1872	1.3302	0.101
H(3)	4e	0.6229	0.2472	1.2886	0.081
H(4)	4e	0.4922	0.2734	1.0640	0.070
H(5)	4e	0.3274	0.2383	0.8703	0.059
H(6)	4e	0.2698	0.2110	0.6400	0.067
H(7)	4e	0.1002	0.2538	0.4865	0.087
H(8)	4e	−0.1532	0.2613	0.4955	0.092
H(9)	4e	−0.2408	0.2253	0.6560	0.089
H(10)	4e	−0.0733	0.1838	0.8177	0.067
H(11)	4e	0.0788	0.0995	0.8189	0.071
H(12)	4e	−0.1016	0.0741	0.9247	0.099
H(13)	4e	−0.1656	0.1072	1.1130	0.096
H(14)	4e	−0.0304	0.1604	1.2079	0.090
H(15)	4e	0.1501	0.1849	1.1021	0.072
H(16)	4e	0.0419	0.143	0.5955	0.078

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(17)	4e	-0.2153	0.1612	0.4601	0.123
H(18)	4e	-0.3949	0.1173	0.3258	0.092
H(19)	4e	-0.3118	0.0576	0.3100	0.069
H(20)	4e	-0.0512	0.0414	0.4273	0.058
H(21)	4e	-0.0458	0.0453	0.6970	0.060
H(22)	4e	-0.0485	-0.0049	0.8504	0.076
H(23)	4e	0.1796	-0.0381	0.9588	0.076

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(24)	4e	0.4158	-0.0200	0.9264	0.066
H(25)	4e	0.4258	0.0318	0.7868	0.050
H(26)	4e	0.2224	0.1069	0.3607	0.078
H(27)	4e	0.2889	0.0834	0.1587	0.092
H(28)	4e	0.3709	0.0249	0.1582	0.085
H(29)	4e	0.3759	-0.0131	0.3543	0.089
H(30)	4e	0.2953	0.0072	0.5531	0.069

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Re(1)	4e	0.39099(2)	0.125563(5)	0.74155(2)	0.03571(9)	0.03181(8)	0.03705(9)	-0.00314(8)	0.01379(6)	0.00318(8)
Br(1)	4e	0.47442(8)	0.09275(2)	0.98160(7)	0.0770(4)	0.0591(4)	0.0590(4)	0.0016(3)	0.0106(3)	0.0046(3)
P(1)	4e	0.2411(1)	0.16355(3)	0.8556(1)	0.0364(6)	0.0269(5)	0.0402(6)	-0.0017(4)	0.0118(5)	0.0020(4)
P(2)	4e	0.2049(1)	0.07877(3)	0.6185(1)	0.0383(6)	0.0284(5)	0.0324(5)	0.0014(4)	0.0101(5)	0.0027(4)
O(1)	4e	0.6239(5)	0.0811(1)	0.6649(6)	0.064(3)	0.086(4)	0.119(4)	0.010(2)	0.052(3)	-0.024(3)
O(2)	4e	0.6452(5)	0.1783(1)	0.8515(6)	0.053(3)	0.066(3)	0.116(4)	-0.025(2)	0.023(3)	-0.007(3)
O(3)	4e	0.3351(5)	0.16123(8)	0.4864(3)	0.076(3)	0.024(2)	0.044(2)	-0.021(2)	0.037(2)	-0.015(1)
C(1)	4e	0.5350(6)	0.0974(1)	0.6861(6)	0.052(3)	0.048(3)	0.053(3)	-0.007(2)	0.022(3)	-0.011(2)
C(2)	4e	0.5507(6)	0.1581(1)	0.8144(6)	0.045(3)	0.054(3)	0.055(3)	-0.015(2)	0.020(2)	-0.006(2)
C(3)	4e	0.3269(8)	0.1524(1)	0.5732(4)	0.081(5)	0.034(3)	0.091(4)	0.003(3)	-0.010(4)	-0.009(3)
C(4)	4e	0.3635(5)	0.1914(1)	0.9918(6)	0.035(2)	0.035(2)	0.052(2)	0.000(2)	0.009(2)	-0.004(2)
C(5)	4e	0.4389(9)	0.1769(2)	1.1210(7)	0.090(5)	0.045(3)	0.059(3)	-0.001(3)	-0.008(3)	0.008(2)
C(6)	4e	0.5297(9)	0.1982(2)	1.2278(8)	0.093(5)	0.066(3)	0.064(4)	-0.003(4)	-0.017(4)	-0.009(3)
C(7)	4e	0.5493(7)	0.2317(2)	1.2056(7)	0.053(4)	0.069(3)	0.071(3)	-0.014(3)	0.005(3)	-0.024(3)
C(8)	4e	0.4775(7)	0.2462(2)	1.0803(7)	0.054(3)	0.045(3)	0.075(3)	-0.012(2)	0.019(3)	-0.017(2)
C(9)	4e	0.3838(6)	0.2264(1)	0.9709(6)	0.040(3)	0.042(2)	0.064(3)	-0.006(2)	0.013(2)	0.001(2)
C(10)	4e	0.1120(6)	0.1951(1)	0.7410(5)	0.041(2)	0.035(2)	0.045(3)	0.004(2)	0.006(2)	0.001(2)
C(11)	4e	0.1586(7)	0.2144(1)	0.6465(7)	0.052(3)	0.048(3)	0.071(4)	0.004(2)	0.023(3)	0.025(2)
C(12)	4e	0.0618(8)	0.2384(2)	0.5587(8)	0.073(4)	0.056(4)	0.077(4)	0.011(3)	0.007(3)	0.029(3)
C(13)	4e	-0.0793(8)	0.2426(2)	0.5629(8)	0.071(4)	0.058(4)	0.083(5)	0.024(3)	-0.002(3)	0.017(3)
C(14)	4e	-0.1274(7)	0.2225(2)	0.6547(8)	0.046(3)	0.077(5)	0.091(5)	0.026(3)	0.010(3)	0.009(3)
C(15)	4e	-0.0341(7)	0.1989(2)	0.7453(7)	0.045(3)	0.061(3)	0.064(4)	0.008(2)	0.020(3)	0.000(3)
C(16)	4e	0.1256(6)	0.1439(1)	0.9503(5)	0.044(3)	0.040(2)	0.042(2)	0.000(2)	0.016(2)	0.007(2)
C(17)	4e	0.0541(8)	0.1131(2)	0.9036(7)	0.075(4)	0.049(3)	0.062(4)	-0.017(3)	0.036(3)	-0.012(3)
C(18)	4e	-0.0488(9)	0.0987(2)	0.9617(8)	0.092(5)	0.089(5)	0.089(5)	-0.045(4)	0.058(4)	-0.009(4)
C(19)	4e	-0.0816(9)	0.1170(2)	1.0700(8)	0.080(5)	0.094(5)	0.083(5)	-0.015(4)	0.049(4)	0.012(3)
C(20)	4e	-0.0082(9)	0.1472(2)	1.1211(8)	0.091(5)	0.086(5)	0.070(4)	-0.001(3)	0.057(4)	0.000(3)
C(21)	4e	0.0941(8)	0.1609(2)	1.0620(6)	0.090(5)	0.048(3)	0.053(3)	-0.005(3)	0.039(3)	-0.007(2)
C(22)	4e	0.0112(5)	0.0913(1)	0.5242(5)	0.041(2)	0.035(2)	0.035(2)	0.001(2)	0.009(2)	0.004(2)
C(23)	4e	-0.0351(7)	0.1243(2)	0.5313(7)	0.062(3)	0.042(2)	0.069(4)	0.011(3)	-0.013(3)	-0.017(3)
C(24)	4e	-0.1809(9)	0.1347(2)	0.457(1)	0.070(4)	0.069(4)	0.120(7)	0.028(3)	-0.040(4)	-0.034(4)
C(25)	4e	-0.2806(8)	0.1101(2)	0.3794(8)	0.059(4)	0.072(3)	0.075(4)	0.020(3)	-0.014(3)	-0.016(3)
C(26)	4e	-0.2338(7)	0.0766(2)	0.3708(6)	0.048(3)	0.062(3)	0.051(3)	-0.005(2)	-0.001(2)	-0.012(3)
C(27)	4e	-0.0887(6)	0.0672(1)	0.4390(6)	0.048(2)	0.048(3)	0.044(3)	-0.005(2)	0.008(2)	-0.012(2)
C(28)	4e	0.1904(6)	0.0418(1)	0.7282(5)	0.051(2)	0.027(2)	0.038(2)	-0.002(2)	0.017(2)	-0.002(1)
C(29)	4e	0.0563(6)	0.0314(1)	0.7478(6)	0.051(3)	0.049(3)	0.051(3)	-0.009(2)	0.019(2)	-0.003(2)
C(30)	4e	0.0546(8)	0.0028(2)	0.8332(7)	0.078(4)	0.061(3)	0.055(3)	-0.024(3)	0.029(3)	0.005(2)
C(31)	4e	0.1830(8)	-0.0156(1)	0.8955(6)	0.094(4)	0.043(3)	0.054(3)	-0.016(3)	0.024(3)	0.012(2)
C(32)	4e	0.3153(7)	-0.0055(1)	0.8775(6)	0.081(3)	0.035(2)	0.041(3)	-0.001(3)	0.006(3)	0.008(2)
C(33)	4e	0.3202(6)	0.0234(1)	0.7967(5)	0.053(3)	0.034(2)	0.033(2)	-0.002(2)	0.006(2)	0.000(2)
C(34)	4e	0.2579(5)	0.0592(1)	0.4744(5)	0.041(2)	0.048(2)	0.032(2)	-0.003(2)	0.013(2)	-0.005(2)
C(35)	4e	0.2551(8)	0.0802(2)	0.3612(6)	0.097(5)	0.056(4)	0.049(3)	-0.006(3)	0.034(3)	0.005(2)
C(36)	4e	0.2944(9)	0.0668(2)	0.2472(7)	0.093(5)	0.098(4)	0.054(4)	-0.015(4)	0.043(4)	-0.009(3)
C(37)	4e	0.3376(7)	0.0345(2)	0.2455(7)	0.054(3)	0.111(4)	0.049(3)	0.005(4)	0.020(3)	-0.022(3)
C(38)	4e	0.3400(8)	0.0134(2)	0.3556(7)	0.078(5)	0.084(5)	0.055(3)	0.028(4)	0.016(3)	-0.021(3)
C(39)	4e	0.2972(7)	0.0248(2)	0.4697(6)	0.064(4)	0.055(3)	0.050(3)	0.016(3)	0.013(3)	0.000(3)

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References

1. Abel, E. W.; Wilkinson, G.: Carbonyl Halides of Manganese and Some Related Compounds. *J. Chem. Soc.* (1959) 1501-1505.
2. Horn, E.; Snow, M. R.: Perchlorate and Difluorophosphate Coordination Derivatives of Rhenium Carbonyl. *Aust. J. Chem.* **33** (1980) 2369-2376.
3. Beck, W.; Suenkel, K.: Metal Complexes of Weakly Coordinating Anions, Precursors of Strong Organometallic Lewis Acids. *Chem. Rev.* **88** (1988) 1405-1421.
4. Horn, E.; Snow, M. R.: Aquo and Perfluoro Anion (BF₄⁻, AsF₆⁻) Coordination Isomers of Manganese and Rhenium Carbonyls. *Aust. J. Chem.* **37** (1980) 1375-1393.
5. Horn, E.; Snow, M. R.: Coordinated Fluoride in Rhenium(I) Carbonyl Complexes. *Aust. J. Chem.* **37** (1987) 35-45.
6. Horn, E.; Snow, M. R.: A Tetranuclear Carbonyl Fluoro Rhenium(I) Cluster, [Re(CO)₃F]₄ · 4H₂O. *Aust. J. Chem.* **34** (1981) 737-743.
7. Horn, E.; Horiluchi, A.: Crystal structure of aquo-(*N,N,N',N'*-1,1,4,4-tetramethylethylenediamine)-tricarbonyl-manganese(I) tetrafluoroborate, [(H₂O)(CO)₃(C₆H₁₆N₂)Mn](BF₄). *Z. Kristallogr. NCS* **216** (2001) 73-74.
8. Cotton, F. A.: Vibrational Spectra and Bonding in Metal Carbonyls. III. Force Constants and Assignments of CO Stretching Modes in Various Molecules; Evaluation of Co Bond Orders. *Inorganic Chemistry* **3** (1964) 702-711.
9. Altomare, G.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.: SIR92-a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **27** (1994) 435-350.
10. Molecular Structure Corporation. teXsan. Single Crystal Structure Analysis Software. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA 1995.
11. Johnson, C. K.: ORTEP-II. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA 1976.