

Tricarbonyl[1,1',1''-ethylidynetris-(pyrazole- κN^2)]rhenium(I) bromide and tricarbonyl[methylidynetris-(pyrazole- κN^2)]rhenium(I) iodide ethanol hemisolvate

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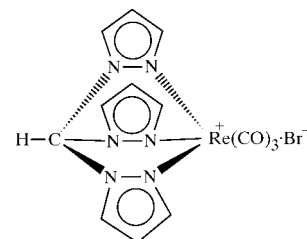
The two title compounds, $[\text{Re}(\text{C}_{10}\text{H}_{10}\text{N}_6)(\text{CO})_3]\text{Br}$ and $[\text{Re}(\text{C}_{11}\text{H}_{12}\text{N}_6)(\text{CO})_3]\text{I}\cdot 0.5\text{C}_2\text{H}_6\text{O}$, have slightly distorted octahedral geometries about the rhenium centers. The distortions result from the constraints of the η^3 -coordinated tris(pyrazol-1-yl)methane ligands in each case which reduce the N—Re—N bond angles well below the preferred value of 90° for facially disposed ligands at a six-coordinate metal center.

Comment

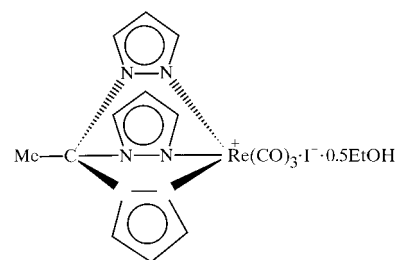
The title compounds, (I) and (II), respectively, have been prepared as part of a general study of ligand systems which are capable of variable denticity. The tris(pyrazol-1-yl)methane ligand $[\text{HC}(\text{pz})_3]$ has previously demonstrated the capacity for either bidentate or tridentate coordination (Macchioni *et al.*, 1998). Flexibility in changing between these two coordination modes may play an important role in catalytic processes, as demonstrated for some of the closely related tris(pyrazol-1-yl)borate complexes (Bromberg *et al.*, 1997). Compounds (I) and (II) have been characterized in order to increase our knowledge of the structural characteristics of metal complexes with this ligand.

An ORTEP-3 diagram (Farrugia, 1997) of (I) is shown in Fig. 1. The constraints of the η^3 -coordinated $\text{HC}(\text{pz})_3$ ligand reduce the N—Re—N bond angles well below the preferred value of 90° . The N—Re—N bond angles in (I) are also smaller [average $81.4(1)^\circ$] than those in $[\text{HC}(3\text{-}^i\text{Prpz})_3\text{Mn}(\text{CO})_3](\text{SO}_3\text{CF}_3)$ (Reger *et al.*, 2000), which average $85.0(3)^\circ$. The C—Re—C bond angles associated with the three facial carbonyl groups in (I) average $88.8(3)^\circ$, whereas the corresponding angles in the Mn complex are slightly greater, with an average of $89.6(5)^\circ$. The constraints of the $\text{HC}(\text{pz})_3$ ligand in (I) also ensure that *trans* arrangements, such as C3—Re—N1, will be well below 180° ; they range from $173.5(2)^\circ$ for C3—Re—N1 to $176.4(2)^\circ$ for C1—Re—N5, and are all bent

toward the $\text{HC}(\text{pz})_3$ ligand. The corresponding angles in the manganese complex are slightly larger, ranging from $175.7(4)$ to $177.7(4)^\circ$, reflecting the influence of the isopropyl substituents at position 3 of the pyrazole ring.



(I)



(II)

An ORTEP-3 diagram (Farrugia, 1997) of (II) is shown in Fig. 2; similar distortions are seen in (II). The bond angles for the *trans* groups, such as C3—Re—N1, are again well below 180° ; they range from $172.8(3)^\circ$ for C2—Re—N3 to $174.8(2)^\circ$ for C3—Re—N1. The N—Re—N bond angles are even smaller in (II) than in (I) [average $80.5(2)^\circ$], but the C—Re—C bond angles associated with the three facial carbonyl groups are slightly larger than the corresponding angles in (I) [average $89.4(4)^\circ$]. Replacement of hydrogen by methyl in

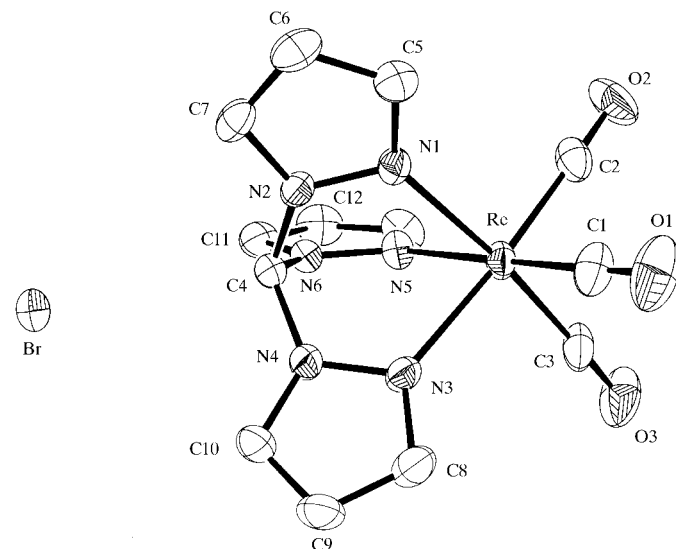


Figure 1
ORTEP-3 (Farrugia, 1997) view of (I) showing 45% displacement ellipsoids. H atoms and the label for C13 have been omitted for clarity.

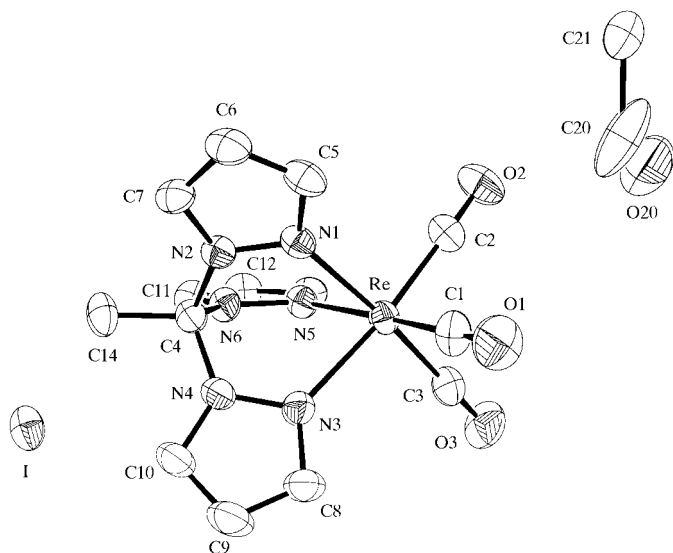


Figure 2
ORTEP-3 (Farrugia, 1997) view of (II) showing 45% displacement ellipsoids. H atoms and the label for C13 have been omitted for clarity.

$\text{CH}_3\text{C}(\text{pz})_3$ does not appear to cause any significant distortions in the complex.

Experimental

The synthesis of (I) was carried out by refluxing $\text{Re}(\text{CO})_5\text{Br}$ and tris(pyrazol-1-yl)methane (1:1) in ethanol for 4 h. Crystals were obtained after allowing the solution to cool overnight to 295 K. Stirring (I) with sodium methoxide (1:1) in methanol for 30 min effected its deprotonation; the neutral product was isolated by evaporation of the solvent followed by extraction into CH_2Cl_2 . Addition of excess CH_3I to this extract, followed by stirring for 4 h, converted the neutral compound to (II). The crude product, (II), was isolated as a colorless solid by evaporating the methylene chloride. Crystals of (II) were obtained by dissolving the product in ethanol and allowing the solution to stand for several days at 253 K.

Compound (I)

Crystal data

$[\text{Re}(\text{C}_{10}\text{H}_{10}\text{N}_6)(\text{CO})_3]\text{Br}$
 $M_r = 564.38$
 Monoclinic, $C2/c$
 $a = 21.565(4) \text{ \AA}$
 $b = 9.002(2) \text{ \AA}$
 $c = 18.396(4) \text{ \AA}$
 $\beta = 105.93(3)^\circ$
 $V = 3434(1) \text{ \AA}^3$
 $Z = 8$
 $D_x = 2.183 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 15.0\text{--}18.0^\circ$
 $\mu = 9.43 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colorless
 $0.33 \times 0.26 \times 0.17 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.07$, $T_{\max} = 0.21$
 4033 measured reflections
 3929 independent reflections
 3172 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 27$
 $k = -11 \rightarrow 0$
 $l = -23 \rightarrow 23$
 3 standard reflections
 frequency: 60 min
 intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.071$
 $S = 1.06$
 3929 reflections
 218 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 1.98P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00343(9)

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Re—C1	1.913 (6)	Re—N1	2.181 (4)
Re—C2	1.911 (5)	Re—N3	2.172 (4)
Re—C3	1.925 (6)	Re—N5	2.175 (4)
C1—Re—C2	89.5 (3)	C2—Re—N5	92.5 (2)
C1—Re—C3	88.6 (3)	C3—Re—N1	173.5 (2)
C2—Re—C3	88.2 (2)	C3—Re—N3	94.4 (2)
C1—Re—N1	96.2 (2)	C3—Re—N5	94.4 (2)
C1—Re—N3	95.1 (2)	N1—Re—N3	80.9 (1)
C1—Re—N5	176.4 (2)	N1—Re—N5	80.6 (1)
C2—Re—N1	96.1 (2)	N3—Re—N5	82.8 (1)
C2—Re—N3	174.8 (2)		

Compound (II)

Crystal data

$[\text{Re}(\text{C}_{11}\text{H}_{12}\text{N}_6)(\text{CO})_3]\text{I} \cdot 0.5\text{C}_2\text{H}_6\text{O}$
 $M_r = 648.44$
 Monoclinic, $P2_1/n$
 $a = 12.361(3) \text{ \AA}$
 $b = 11.803(2) \text{ \AA}$
 $c = 15.543(3) \text{ \AA}$
 $\beta = 108.83(3)^\circ$
 $V = 2146.3(7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.022 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 15.0\text{--}18.0^\circ$
 $\mu = 7.13 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colorless
 $0.41 \times 0.23 \times 0.23 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.08$, $T_{\max} = 0.20$
 5073 measured reflections
 4896 independent reflections
 4128 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$
 $\theta_{\max} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 20$
 3 standard reflections
 frequency: 60 min
 intensity decay: <2%

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Re—C1	1.901 (8)	Re—N1	2.168 (5)
Re—C2	1.920 (7)	Re—N3	2.169 (5)
Re—C3	1.922 (8)	Re—N5	2.152 (6)
Re—N5	2.152 (6)		
C1—Re—C2	91.1 (3)	C2—Re—N5	92.9 (3)
C1—Re—C3	89.0 (3)	C3—Re—N5	95.2 (3)
C2—Re—C3	87.8 (3)	C3—Re—N3	96.0 (2)
C1—Re—N1	94.8 (3)	C3—Re—N1	174.8 (2)
C1—Re—N3	95.1 (3)	N1—Re—N3	80.17 (18)
C1—Re—N5	174.3 (3)	N1—Re—N5	80.77 (19)
C2—Re—N1	95.6 (3)	N3—Re—N5	80.7 (2)
C2—Re—N3	172.8 (3)		

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.12$
 4896 reflections
 254 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 1.9504P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.014$
 $\Delta\rho_{\max} = 1.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.29 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0094 (5)

The H-atom positions for both compounds were calculated and their refinement was constrained with C–H = 0.93–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the pyrazole, methylene and methine H atoms. For the methyl groups, the torsion angle which defined the orientation was not allowed to refine, and these atoms were assigned $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The occupancy factor of the ethanol solvate was varied during the initial stages of the refinement; since the value converged to about 0.5 it was set at 0.5 for the final cycles. The highest peak in (I) is located 0.93 Å from Re, 1.39 Å from C1 and 1.93 Å from N3, and the deepest trough is 0.98 Å from Re and 1.35 Å from N5. In (II), the highest peak and deepest trough are 1.24 Å from Re and 1.02 Å from C2, respectively.

For both compounds, data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1610). Services for accessing these data are described at the back of the journal.

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