alternating layers, related by inversion, offset with respect to each other. The average intermolecular distance between the C and O atoms of the naphthopyran rings related in this manner is 3.5 (1) Å. The layers are connected by pairs of hydrogen bonds formed between the carboxyl groups, as well as those involving the water molecules. Inversion centers along the *c* axis relate pairs of coordinated Na ions which lie near this axis. Hydrogen bonding between the carboxylic acid groups occurs perpendicular to the *z* direction and separates from each other the Na ion pairs created by coordination and related by the inversion centers.

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Structures of $[(L)(CO)_4ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (L = CO, ^{t}BuNC)

BY WAYNE L. INGHAM, S. DON TRAVLOS, JAN C. A. BOEYENS, MARK BERRY AND NEIL J. COVILLE*

Applied Chemistry and Chemical Technology Centre, Department of Chemistry,
University of the Witwatersrand, PO WITS 2050, Johannesburg, Republic of South Africa

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Abstract. Octacarbonyl-1κ^5C,2κ^3C-2(η^5)-cyclopentadienemolybdenumrhenium(*Mo—Re*), $[(CO)_5ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (*A*), M_r = 571.2, monoclinic, $P2_1/c$, a = 7.046 (1), b = 24.967 (2), c = 9.174 (1) Å, β = 107.95 (2)°, V = 1535.2 Å^3, Z = 4, D_x = 2.47 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 88.2 cm^{-1}, F(000) = 1056.0, T = 293 K, R = 0.037 for 2028 unique reflections. (*tert*-Butyl isocyanide-2κC)-heptacarbonyl-1κ^4C,2κ^3C-2(η^5)-cyclopentadienemolybdenumrhenium(*Mo—Re*), $[(^tBuNC)(CO)_4ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (*B*), M_r = 626.3, triclinic, $P\bar{1}$, a = 7.108 (4), b = 9.731 (1), c = 14.240 (2) Å, α = 90.247 (6), β = 89.969 (5), γ = 87.297 (5)°, V = 983.9 Å^3, Z = 2, D_x = 1.054 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 34.3 cm^{-1}, F(000) = 593.8, T = 293 K, R = 0.024 for 5240 unique reflections. The ^{t}BuNC ligand is found attached to the Re atom in an equatorial site in (*B*). The ^{t}BuNC group in (*B*) is found to influence the *M*—CO bond lengths on *both* the Mo and Re atoms relative to (*A*). In both structures the group(s) on Re closest to the C_5H_5 ring on Mo bends in towards the C_5H_5 ring.

Introduction. Little information is available on the substitution chemistry of mixed metal dimer carbonyl complexes (Roberts & Geoffrey, 1982) and in particular on the site of attachment of an incoming ligand to the metal dimer. While investigating the CO substitution reactions of $[(\eta^5\text{-}C_5H_5)MoM(CO)_8]$ (M = Mn, Re) with isocyanides we observed that the products obtained were influenced by the Group 7 metal. Thus, reaction with M = Mn (Ingham, Billing,

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* To whom correspondence should be addressed.

Levendis & Coville, 1991) yielded [(η^5-C$_5$H$_5$)-Mo(CO)$_3$]$_2$ (Wilkinson, 1954) and [Mn$_2$(CO)$_8$-(^{t}BuNC)$_2$] (Albers & Coville, 1982) while reaction with M = Re gave a dimer substituted product [(η^5-C$_5$H$_5$)MoRe(CO)$_7$(^{t}BuNC)] (Ingham & Coville, 1992). To permit understanding of these differing results we have carried out the crystal structure determinations of [(η^5-C$_5$H$_5$)MoRe(CO)$_7$(L)] [L = CO (A), ^{t}BuNC (B)]. It is to be noted that some earlier crystallographic data have been reported for [(η^5-C$_5$H$_5$)MoRe(CO)$_8$] (Struchkov, Anisimov, Osipova, Kolobova & Nesmeyanov, 1967).

Experimental. (A) was obtained from the reaction between [Re(CO)$_5$(SO$_3$CF$_3$)] (Nitschke, Schmidt & Trogler, 1985) and Na[(η^5-C$_5$H$_5$)Mo(CO)$_3$] (Hayter, 1963) while (B) was prepared from the reaction of (A) with ^{t}BuNC in the presence of PdO catalyst (Ingham & Coville, 1992). Both (A) and (B) were purified by column chromatography and orange crystals suitable for X-ray analysis were obtained by slow crystallization of the materials from CH$_2$Cl$_2$/hexane mixtures at 273 K.

(A): Crystal 0.55 × 0.30 × 0.15 mm, photography established space group $P2_1/c$, Nonius CAD-4 four-circle diffractometer. Mo $K\alpha$ graphite-monochromated radiation, ω–2θ scan [scan width (0.80 − 0.35tanθ)°, scan speed 5.49° min^{-1}], $3 < \theta < 30°$, h 0–6, k −24–24, l 0–8, cell constants from least-squares refinement of the θ values of 25 general reflections, 4157 intensities measured, 2028 reflections with $I > 4\sigma(I)$.

(B): Crystal 0.52 × 0.33 × 0.24 mm, photography established space group $P\bar{1}$, Nonius CAD-4 four-circle diffractometer. Mo $K\alpha$ graphite-monochromated radiation, ω–2θ scan [scan width (0.80 − 0.35tanθ)°, scan speed 5.49° min^{-1}], $3 < \theta < 30°$, h −9–9, k −13–13, l 0–19, cell constants from least-squares refinement of the θ values of 25 general reflections, 5935 intensities measured, 5240 reflections with $I > 3\sigma(I)$.

For both structures Lorentz–polarization and empirical absorption corrections [max., min. transmission factors 99.92, 41.86% for (A), 99.86, 68.74% for (B)] were applied. Linear and approximate isotropic crystal decay was minor and no correction was made for this during processing.

Patterson (Re, Mo atoms) and difference Fourier techniques were employed to solve the structures using normal heavy-atom procedures. Full-matrix least-squares refinement (on F) (*SHELX*82; Sheldrick, 1982) with all non-H atoms anisotropic and H atoms in calculated positions was performed. During refinement of (B) unaccounted electron density was observed in the region of the C$_5$H$_5$ ring. This unaccounted electron density was attributed to rotational disorder of the C$_5$H$_5$ ring. A model with idealized C$_5$H$_5$ rings as regular pentagons with each atom in each ring assigned $\frac{1}{2}$ site occupancy was used and the pentagons were refined as rigid bodies.

The weighting scheme used for both (A) and (B) was $w = [K\sigma^2(F)]^{-1}$. Final R and wR for (A) are 0.037 and 0.027, and for (B) 0.024 and 0.023.* Max. $\Delta/\sigma = 0.017$ for (A), 0.015 for (B). 207 refined parameters for (A), 231 for (B). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and anomalous-dispersion corrections for Mo and Re from Cromer & Liberman (1970). Residual electron density in the final difference maps was within 0.94 and −1.0 e Å^{-3} for (A) and 0.86 and −1.6 e Å^{-3} for (B).

Discussion. The stereochemistries of (A) and (B) are illustrated by *ORTEP* (Johnson, 1965) plots in Figs. 1 and 2 respectively, which also show the numbering schemes used in the analyses. Table 1 contains the positional and thermal parameters of (A) and (B)

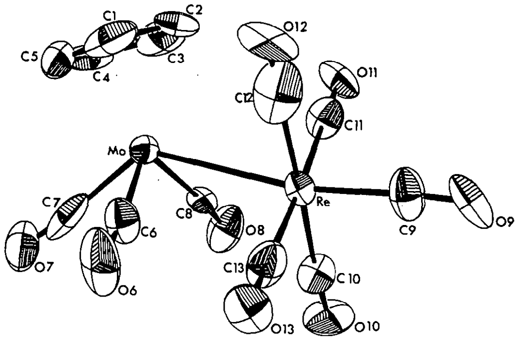

Fig. 1. An *ORTEP* (Johnson, 1965) plot of structure (A) showing the numbering system used. (H atoms omitted.)

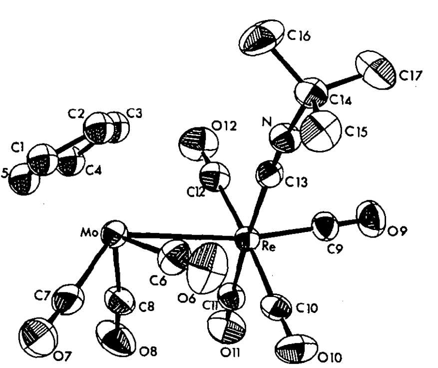

Fig. 2. An *ORTEP* (Johnson, 1965) plot of structure (B) showing the numbering system used. (H atoms omitted.)

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* Lists of structure factors, bond lengths and angles, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54650 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for* (*A*) *and* (*B*) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
(*A*)				
Mo	−687 (2)	1087 (0)	1287 (2)	38 (0)
Re	772 (1)	1427 (0)	4789 (1)	44 (0)
C1	−3503 (36)	659 (8)	−283 (28)	78 (5)
C2	−3866 (32)	691 (8)	1126 (31)	74 (5)
C3	−4050 (27)	1255 (7)	1431 (28)	65 (4)
C4	−3752 (29)	1558 (7)	206 (26)	61 (4)
C5	−3463 (28)	1180 (10)	−871 (23)	76 (5)
C6	975 (33)	492 (6)	2469 (21)	60 (4)
C7	951 (33)	833 (6)	−126 (24)	59 (4)
C8	1078 (23)	1716 (6)	1476 (18)	48 (3)
C9	1200 (39)	1709 (7)	6842 (21)	69 (4)
C10	3330 (30)	1794 (6)	4662 (23)	60 (4)
C11	−883 (29)	2069 (5)	3790 (21)	57 (4)
C12	−1918 (41)	1010 (7)	4900 (28)	71 (5)
C13	2397 (31)	759 (6)	5682 (21)	57 (4)
O6	1855 (31)	121 (5)	2978 (17)	87 (4)
O7	1660 (32)	663 (6)	−950 (19)	103 (4)
O8	2120 (23)	2083 (4)	1333 (16)	83 (3)
O9	1559 (32)	1906 (6)	7963 (21)	105 (0)
O10	4716 (20)	1998 (6)	4681 (22)	93 (4)
O11	−1872 (21)	2415 (4)	3286 (18)	72 (3)
O12	−3238 (28)	804 (6)	5002 (30)	120 (0)
O13	3283 (23)	399 (5)	6197 (15)	65 (3)
(*B*)				
Mo	909 (1)	2510 (1)	3718 (0)	36 (0)
Re	681 (0)	2232 (0)	1493 (0)	31 (0)
C1	3752 (22)	3692 (14)	3875 (11)	48 (1)
C2	4276 (22)	2281 (14)	3535 (11)	48 (1)
C3	3771 (20)	1297 (16)	4164 (10)	48 (1)
C4	3009 (20)	1958 (14)	4936 (10)	48 (1)
C5	2990 (21)	3384 (15)	4804 (10)	48 (1)
C6	−395 (9)	843 (7)	3407 (4)	42 (2)
C7	−1112 (9)	2580 (8)	4629 (5)	55 (2)
C8	−723 (9)	4038 (7)	3226 (4)	54 (1)
C9	949 (8)	1823 (6)	188 (4)	45 (1)
C10	−1808 (8)	1399 (6)	1549 (4)	44 (1)
C11	−648 (8)	4003 (6)	1196 (4)	45 (1)
C12	3098 (9)	3155 (6)	1502 (5)	44 (1)
C13	2023 (7)	315 (5)	1753 (4)	36 (1)
C14	3500 (9)	−2170 (6)	1932 (5)	46 (1)
C15	1917 (10)	−3028 (6)	2317 (5)	49 (2)
C16	5170 (10)	−2160 (7)	2597 (6)	67 (2)
C17	4096 (11)	−2608 (7)	947 (5)	88 (2)
C′1	3390 (20)	1363 (16)	4489 (10)	48 (1)
C′2	2823 (19)	2518 (14)	5052 (10)	48 (1)
C′3	3164 (20)	3759 (15)	4551 (10)	48 (1)
C′4	4002 (21)	3308 (15)	3722 (11)	48 (1)
C′5	4158 (22)	1872 (14)	3658 (12)	48 (1)
N	2727 (7)	−756 (5)	1855 (3)	42 (1)
O6	−1087 (8)	−200 (5)	3321 (4)	52 (2)
O7	−2268 (7)	2596 (7)	5196 (4)	94 (2)
O8	−1697 (7)	4979 (5)	3053 (4)	99 (2)
O9	1117 (7)	1547 (5)	−586 (3)	75 (1)
O10	−3253 (6)	938 (5)	1532 (4)	60 (1)
O11	−1390 (7)	4999 (4)	959 (3)	66 (1)
O12	4470 (7)	3721 (5)	1457 (4)	62 (1)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *for* (*A*) *and* (*B*) *with e.s.d.'s in parentheses*

	(*A*)	(*B*)
Mo—Re	3.172 (1)	3.188 (1)
Mo—$C_{\text{Ring av.}}$	2.380 (25)	2.377 (11)
Mo—C6	1.994 (14)	1.959 (5)
Mo—C7	2.083 (33)	1.924 (5)
Mo—C8	1.978 (16)	1.980 (4)
Re—C9	1.946 (21)	1.906 (4)
Re—C10	2.057 (24)	1.984 (4)
Re—C11	2.027 (13)	1.977 (4)
Re—C12	2.192 (13)	1.978 (4)
Re—C13	2.046 (14)	2.093 (4)
C—$C_{\text{Ring av.}}$	1.42 (4)	1.42 (1)
C6—Mo—Re	72.3 (5)	71.0 (1)
C7—Mo—Re	130.0 (3)	128.6 (1)
C8—Mo—Re	72.6 (5)	70.8 (1)
C6—Mo—C7	76.5 (9)	78.4 (2)
C7—Mo—C8	80.9 (7)	78.7 (2)
C8—Mo—C6	107.3 (7)	104.7 (2)
C9—Re—Mo	169.3 (7)	169.0 (1)
C10—Re—Mo	94.5 (6)	93.1 (1)
C11—Re—Mo	78.0 (5)	100.0 (1)
C12—Re—Mo	84.6 (7)	84.1 (1)
C13—Re—Mo	98.9 (5)	82.4 (1)
C9—Re—C10	91.0 (1)	91.5 (2)
C9—Re—C11	92.7 (8)	90.2 (2)
C9—Re—C12	90.0 (1)	91.6 (2)
C9—Re—C13	90.4 (7)	87.6 (2)

and Table 2 contains selected bond distances and angles.

The main features observed on comparison of the two structures, (*A*) and (*B*), are described below:

(i) Substitution of the CO group has occurred on Re in an equatorial site (Fig. 2).

(ii) The structures have very similar geometries with two CO ligands being nearly eclipsed [C13, C6 in (*A*), C11, C8 in (*B*)] in both structures (Fig. 3).

(iii) The Mo—Re bond length increases on substitution of a CO group by ^{t}BuNC (3.172 to 3.188 Å). [In an earlier report (Struchkov, Anisimov, Osipova, Kolobova & Nesmeyanov, 1967) a value of 3.12 Å was reported for the Mo—Re bond length.] This bond length is to be compared with Mo—Re = 3.111 (2) Å for [Re(CO)$_5$Mo(CO)$_4$(CPh)] (Fischer, Huttner, Lindner, Frand & Kreissel, 1976). All other reported structures of dimers containing an Re—Mo bond also contain a bridging group and the Re—Mo bond lengths are consequently much shorter. Structures include: [(η^5-C$_5$H$_5$)$_2$Mo(μ-CO)$_2$Re(CO)-(η^5-C$_5$H$_5$)], Mo—Re = 2.959 (1) Å (Mink, Welter, Young & Stuckey, 1979); [(η^5-C$_5$H$_5$)Mo(μ-CO)-(μ-CMeCMe)Re(CO)$_3$(PPh$_3$)], Mo—Re = 2.943 (2) Å, and [(η^5-C$_5$H$_5$)Mo(μ-CO)(μ-CPhCPh)-Re(CO)$_3$P(OMe$_3$)], Mo—Re = 2.959 (3) Å (Beck, Müller & Nagel, 1986). This is also revealed in the bridged trimer complex [Re$_2$Mo(η^5-C$_5$H$_5$)(CO)$_8$]-[Mo(η^5-C$_5$H$_5$)(CO)$_3$], Mo—Re = 2.909 (2) Å (Vergamini, Vahrenkamp & Dahl, 1971).

(iv) Although the Mo—C6 and Mo—C8 bond lengths are relatively unaffected by substitution of CO by ^{t}BuNC, the Mo—C7 bond which is *trans* to the Mo—Re bond shortens (2.08 to 1.92 Å) on going from (*A*) to (*B*). This suggests that Re(CO)$_4$*R*NC is a poorer π-accepting fragment than the Re(CO)$_5$ fragment.

(v) Significant shortening is observed for all equatorial Re—CO bonds in (*B*) relative to (*A*). This effect is a result of the better σ-donating, poorer π-accepting capacity of the ^{t}BuNC group relative to CO.

(vi) The Re—Mo—CO angles are near equivalent in (*A*) and (*B*) and this relates to the steric compactness associated with the seven-coordinate Mo atom.

(vii) The Mo—Re—CO bond angles differ slightly in the two structures. It is also to be noted that the ligands on Re, closest to the C_5H_5 ring on Mo, bend in towards the C_5H_5 ring [(*A*) Mo—Re—C11 = 78, Mo—Re—C12 = 84°; (*B*) Mo—Re—C12 = 84, Mo—Re—C13 = 83°] (Fig. 3). This bending is a consequence of the relatively small size of the C_5H_5 ligand relative to the three CO ligands (du Plooy, Pickl & Coville, 1992).

(viii) The Mo—Re—C9 angle in both structures is 169°. However, C9 is perpendicular to a plane containing the four equatorial Re ligands (CO, ^{t}BuNC) with C9 bending towards the side of the molecule which contains the C_5H_5 group (Fig. 3).

The crystallographic data show that addition of ^{t}BuNC to (*A*) results in Mo—Re bond lengthening, as a result of either steric or electronic effects. Substitution of a CO ligand on Mn in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5]$ (*C*) by ^{t}BuNC to give $[(\eta^5\text{-}C_5H_5)MoMn(CO)_7(^t\text{BuNC})]$ (*D*) can be expected to give a similar increase in the Mo—Mn bond length relative to the starting material. On electronic grounds the influence of the ^{t}BuNC group in (*B*) and (*C*) should be similar. However, since the Mo—Mn bond in (*C*) is much shorter than the Mo—Re bond in (*A*), the steric interaction of the ^{t}BuNC in (*D*) with the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ fragment can be expected to be more severe than in (*B*). This would give rise to the bond homolysis which is observed (Ingham, Billing, Levendis & Coville, 1991) and implies that steric factors associated with ligands in metal dimers will play an important role in determining metal dimer stability.

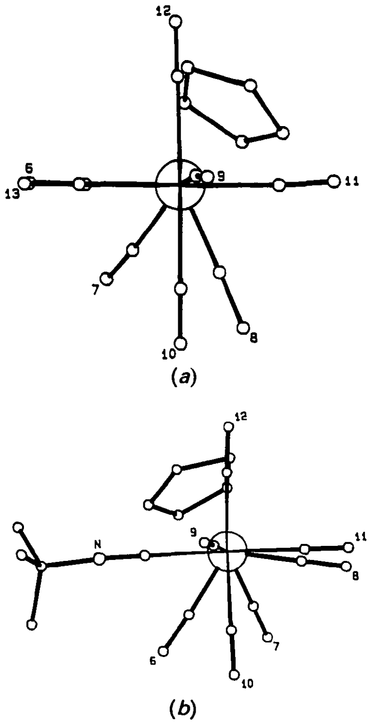

Fig. 3. Projection down the Re—Mo bond of (*a*) structure (*A*) and (*b*) structure (*B*). (H atoms omitted.)

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