dominant if not exclusive reaction occurs with no Re–Re bond cleavage and is consistent with similar results obtained for the reaction between $[Mn_2(CO)_{10}]$ and *t*-BuNC in the presence of Pd/C as catalyst[9c] and hence rules out the radical substitution process (Scheme Ia) for the catalyzed reaction. The results do not however indicate whether the catalyzed reaction occurs via an associative process or dissociate process similar to the uncatalyzed reaction, and further kinetic investigations will be needed to establish this feature of the mechanism.

Reaction of $[Re_2(CO)_{10}]$ and 2 equiv of *t*-BuNC in the presence of $Pd/CaCO_3$ leads exclusively to 1,2-*dieq*-$[Re_2(CO)_8(CNBu\text{-}t)_2]$. Attempts to isomerize this complex to the 1,1 isomer (125 °C, 6 h) in both the presence and absence of catalyst failed.[29] The 1,1 isomer, independently synthesized from $Na[Re(CO)_5]$ and $Re(CO)_3(CNBu\text{-}t)_2I$, also failed to isomerize to the 1,2 isomer in both the presence and absence of the $Pd/CaCO_3$ catalyst. The 1,2 isomer is thus the kinetic product of the catalyzed reaction. This product could, however, arise from the loss of the two CO groups either from the same[9a] or different Re atoms and would depend on the cis-labilizing effects[33] of the ligands and metal carbonyl fragments.

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Registry No. $[Re_2(CO)_9(CNBu\text{-}t)]$, 79138-90-2; 1,2-$[Re_2(CO)_8(CNBu\text{-}t)_2]$, 95672-44-9; 1,1-$[Re_2(CO)_8(CNBu\text{-}t)_2]$, 95590-05-9; $[Re_2(CO)_7(CNBu\text{-}t)_3]$, 95590-06-0; $[Re_2(CO)_9(CNCH_2C_6H_5)]$, 95590-07-1; $[Re_2(CO)_8(CNCH_2C_6H_5)_2]$, 95590-08-2; $[Re_2(CO)_7(CNCH_2C_6H_5)_3]$, 95590-09-3; $[Re_2(CO)_9(CNC_6H_{11})]$, 95590-10-6; $[Re_2(CO)_8(CNC_6H_{11})_2]$, 95590-11-7; $[Re_2(CO)_7(CNC_6H_{11})_3]$, 95590-12-8; $[Re_2(CO)_9(CNC_6H_3Me_2\text{-}2,6)]$, 95590-13-9; $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$, 95406-94-3; $[Re_2(CO)_7(CNC_6H_3Me_2\text{-}2,6)_3]$, 95590-14-0; $[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$, 95590-15-1; $[Re_2(CO)_9(CNMe)]$, 95672-45-0; 1,1-$[Re_2(CO)_8(CNMe)_2]$, 95590-16-2; 1,2-$[Re_2(CO)_8(CNMe)_2]$, 95590-17-3; $[Re_2(CO)_7(CNMe)_3]$, 95406-95-4; $[Re_2(CO)_6(CNMe)_4]$, 95590-18-4; $[Re_2(^{13}CO)_9(CNBu\text{-}t)]$, 95590-19-5; $[Re_2(CO)_{10}]$, 14285-68-8; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 38117-54-3; 1,1-$[Mn_2(CO)_8(CNBu\text{-}t)_2]$, 94901-45-8; 1,2-$[Mn_2(CO)_8(CNBu\text{-}t)_2]$, 95672-46-1; $[Re_2(^{13}CO)_{10}]$, 95590-20-8; $Na[Re(CO)_3(CNBu\text{-}t)_2]$, 95590-21-9; $[Re(CO)_5I]$, 13821-00-6; $[Re_2(CO)_8(CNBu\text{-}t)(CNC_6H_3Me_2\text{-}2,6)]$, 95590-22-0; PdO, 1314-08-5; $CaCO_3$, 471-34-1; $BaCO_3$, 513-77-9; $BaSO_4$, 7727-43-7; Al_2O_3, 1344-28-1; $CoCl_2$, 7646-79-9; $IrCl_3$, 10025-83-9; K_2PtCl_4, 10025-99-7; $PtBr_2$, 13455-12-4; PtO_2, 1314-15-4; $LiAlH_4$, 16853-85-3; *t*-BuNC, 7188-38-7; $C_6H_5CH_2NC$, 10340-91-7; $C_6H_{11}NC$, 931-53-3; 2,6-$Me_2C_6H_3NC$, 2769-71-3; MeNC, 593-75-9; Pd, 7440-05-3; Pt, 7440-06-4; Zn, 7440-66-6; Rh, 7440-16-6; Ru, 7440-18-8; Re, 7440-15-5; C, 7440-44-0.

Supplementary Material Available: Tables of mass spectra data for $[Mn_2(CO)_8(CNBu\text{-}t)_2]$ and 1,2-$[Re_2(CO)_8(CNBu\text{-}t)_2]$ (3 pages). Ordering information is given on any current masthead page.

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Systematic Substitution of $[Re_2(CO)_{10}]$. The Crystal and Molecular Structure of a Series of $[Re_2(CO)_{10-n}(CNR)_n]$ Complexes ($n = 1$, R = *t*-Bu; $n = 2, 4$, R = 2,6-$Me_2C_6H_3$; $n = 3$, R = Me)

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The crystal and molecular structures of a series of isocyanide derivatives of $Re_2(CO)_{10}$ have been determined. $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$: space group $P\bar{1}$, $Z = 2$, $a = 15.145$ (7) Å, $b = 9.294$ (4) Å, $c = 10.328$ (4) Å, $\alpha = 92.70$ (3)°, $\beta = 74.47$ (2)°, $\gamma = 98.85$ (3)°. $[Re_2(CO)_7(CNMe)_3]$: $P2_1/n$, $Z = 4$, $a = 10.874$ (5) Å, $b = 16.175$ (7) Å, $c = 10.711$ (5) Å, $\beta = 90.07$ (3)°. $[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$: *Pccn*, $Z = 4$, $a = 13.832$ (6) Å, $b = 11.322$ (5) Å, $c = 26.401$ (11) Å. The structures were refined to R values of 0.039, 0.060, and 0.110, respectively. A redetermination of the structure of $[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$ to include absorption corrections yielded an R value of 0.051. In all four structures, the ligand conformation was found to be staggered when viewed down the Re–Re bond with the isocyanide ligands occupying cis-equatorial positions. An increase in the Re–Re bond length in $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 1–4) with increasing degree of isocyanide substitution was only observed when $n = 4$, and this could be ascribed to steric rather than electronic factors.

Introduction

$[Re_2(CO)_{10}]$ and $[Mn_2(CO)_{10}]$ are examples of metal dimers, and their ready availability and moderate air stability have resulted in extensive studies of their chemical and physical properties.[1] Both compounds have been characterized by single-crystal X-ray diffraction techniques,[2-4] and in both instances the structures contain a single long metal–metal bond, no bridging carbonyls, and

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Table I. Crystal Data and Details of the Structure Analysis for the [$Re_2(CO)_{10-n}(CNR)_n$] (n = 2-4) Complexes (II-IV)

	II	III	IV
complex	[$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$]	[$Re_2(CO)_7(CNMe)_3$]	[$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$]
formula	$Re_2C_{26}H_{10}N_2O_8$	$Re_2C_{13}H_9N_3O_7$	$Re_2C_{42}H_{36}N_4O_6$
M_r	850.76	691.63	1065.15
color, shape	cream, needles	yellow, cylindrical	yellow, rectangular
cryst dimens, mm	0.20 × 0.12 × 0.10	0.20 × 0.19 × 0.14	0.60 × 0.40 × 0.40
space group	$P\bar{1}$	$P2_1/n$	$Pccn$
a, Å	15.145 (7)	10.874 (5)	13.832 (6)
b, Å	9.294 (4)	16.175 (7)	11.322 (5)
c, Å	10.328 (5)	10.711 (5)	26.401 (11)
α, deg	92.70 (3)	90	90
β, deg	74.47 (2)	90.07 (3)	90
γ, deg	98.85 (3)	90	90
U, Å^3	1383.94	1883.92	4134.55
Z	2	4	4
$F(000)$	807.80	1255.61	2055.61
D_{calcd}, g cm^{-3}	2.04	2.44	1.71
μ, cm^{-1}	84.10	123.37	104.37
λ, Å	0.7107 (Mo Kα)	0.7107 (Mo Kα)	1.5418 (Cu Kα)
scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
range, deg	$3 \leqslant \theta \leqslant 23$	$3 \leqslant \theta \leqslant 26$	$3 \leqslant \theta \leqslant 68$
scan width, deg	1.40	1.30	1.60
scan speed, deg s^{-1}	0.047	0.043	0.053
range of hkl	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$+h, +k, +l$
measd intensities	3815	3828	3470
unique reflctns	3749	3631	3052
internal consistency R index[a]	0.0117	0.0000	0.0000
omitted reflctns	347	236	160
cutoff criterion	$F < \sigma(F)$	$F < \sigma(F)$	$F < \sigma(F)$
R[b]	0.0386	0.0596	0.1090
R_w[c]	0.0334	0.0467	0.1112

[a] $R = [\Sigma(N\,\Sigma(w(F(\text{mean}) - F)^2))/\Sigma((N-1)(wF^2))]^{1/2}$ where the inner summations are over the N equivalent reflections averaged to give F(mean), and the outer summations are over all unique reflections. [b] The conventional R is defined by $R = \Sigma|F_o - F_c|/\Sigma|F_o|$, where F_o is the observed structure factor and F_c the calculated structure factor. [c] The weighted R is defined by $R_w = \Sigma|(w)^{1/2}(F_o - F_c)|/\Sigma|(w)^{1/2}F_o|$, where $w = 1/\sigma^2(F)$.

a staggered arrangement of the eight equatorial carbonyl ligands. These dimers thus provide a simple model system for the investigation of the chemistry of higher nuclearity clusters.

Although numerous aspects of the chemistry of the $M_2(CO)_{10}$ dimers have been investigated[1] since their initial synthesis and characterization,[5,6] little attempt has been made to investigate systematically the effect of the degree of CO substitution by ligands L on the physical and chemical properties of the metal dimer. There are a number of factors that have been responsible for this situation. First, most studies of the substitution of CO by ligands L to give [$M_2(CO)_{10-n}(L)_n$] ($n > 0$) have been carried out with L = group 5 donor ligands, and consequently steric effects have limited the degree of substitution.[8] Second, the CO groups are nonlabile with respect to substitution, and consequently forcing conditions are required to synthesize the required substituted complexes.[9] Finally, as a result of the high-temperature conditions required for thermal CO substitution, competing pathways including metal-metal bond cleavage can occur resulting in product decomposition.

In this publication we wish to report on an X-ray crystallographic study of a series of [$Re_2(CO)_{10-n}(CNR)_n$] (n = 1-4) complexes, synthesized via catalytic procedures[10] as outlined in the preceding publication.[11] One of the objectives of the study was to establish the stereochemistry of the n = 1-4 isocyanide derivatives. The second objective was to obtain bond length and bond angle data for the complexes and to ascertain the effects of systematic increased isocyanide substitution on these properties. In particular we wished to determine whether systematic increased substitution by the electron-releasing RNC ligand (relative to CO) resulted in a marked change in the Re-Re bond length. This result should have implications for the study of metal clusters in general.

The crystal structure determination of [$Re_2(CO)_9$(CN-*t*-Bu)] has previously been reported.[12] Since the publication of the X-ray data for [$Re_2(CO)_9$(CN-*t*-Bu)], we have applied an absorption correction and the corrected data are contained in the supplementary material. No previous structural information on [$Re_2(CO)_{10-n}(CNR)_n$] ($n > 1$) derivatives has appeared in the literature.

Experimental Section

The synthesis of the complexes [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] (II), [$Re_2(CO)_7(CNMe)_3$] (III), and [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$] (IV) have been reported.[11] Crystals of the complexes were grown under nitrogen at 20 °C from solutions of dichloromethane-hexane (II, IV) or benzene-hexane (II).

In each case preliminary investigation was carried out by using standard Weissenberg and precession photography. Refined cell constants were obtained during data collections on a Phillips PW1100 four-circle diffractometer at 20 °C using Mo K α (II, IV) or Cu K α (IV) graphite-monochromated radiation. Lorentz and

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Table II. Final Atomic Coordinates for $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ (II)[a]

atom	*x/a*	*y/b*	*z/c*
Re(1)	0.3591 (1)	−0.2532 (1)	−0.0150 (1)
Re(2)	0.1661 (1)	−0.1993 (1)	−0.0172 (1)
N(1)	0.3659 (5)	−0.4271 (9)	−0.2913 (8)
N(2)	0.0923 (5)	−0.2582 (9)	0.2985 (8)
O(1)	0.4388 (5)	0.0250 (9)	−0.1890 (9)
O(2)	0.5479 (4)	−0.3179 (9)	0.0029 (8)
O(3)	0.2546 (5)	−0.5381 (8)	0.1347 (7)
O(4)	0.3248 (5)	−0.0727 (9)	0.2497 (8)
O(5)	0.1273 (5)	−0.5267 (8)	−0.0846 (9)
O(6)	0.2334 (5)	0.1202 (8)	0.0551 (8)
O(7)	0.2449 (5)	−0.1250 (8)	−0.3191 (7)
O(8)	−0.0316 (4)	−0.1566 (8)	−0.0144 (8)
CN(1)	0.3619 (6)	−0.3657 (10)	−0.1902 (10)
CN(2)	0.1201 (6)	−0.2407 (10)	0.1858 (10)
CO(1)	0.4097 (7)	−0.0743 (12)	−0.1234 (10)
CO(2)	0.4785 (7)	−0.2925 (11)	−0.0091 (10)
CO(3)	0.2917 (6)	−0.4323 (12)	0.0820 (10)
CO(4)	0.3391 (7)	−0.1372 (12)	0.1534 (11)
CO(5)	0.1420 (6)	−0.4063 (12)	−0.0586 (10)
CO(6)	0.2076 (6)	0.0065 (12)	0.0286 (10)
CO(7)	0.2163 (6)	−0.1522 (11)	−0.2092 (11)
CO(8)	0.0418 (7)	−0.1711 (11)	−0.0135 (10)
C(1)	0.3652 (6)	−0.5109 (11)	−0.4124 (10)
C(2)	0.3346 (7)	−0.6574 (12)	−0.3946 (11)
C(3)	0.3335 (8)	−0.7459 (14)	−0.5155 (13)
C(4)	0.3663 (9)	−0.6696 (15)	−0.6388 (13)
C(5)	0.3979 (7)	−0.5295 (13)	−0.6546 (11)
C(6)	0.3984 (7)	−0.4386 (12)	−0.5377 (11)
C(7)	0.3029 (7)	−0.7330 (13)	−0.2585 (11)
C(8)	0.4292 (8)	−0.2778 (14)	−0.5409 (12)
C(9)	0.0401 (6)	−0.2632 (11)	0.4344 (10)
C(10)	−0.0419 (7)	−0.2003 (12)	0.4667 (11)
C(11)	−0.0917 (8)	−0.2064 (14)	0.6053 (12)
C(12)	−0.0636 (8)	−0.2734 (14)	0.6959 (12)
C(13)	0.0169 (8)	−0.3395 (14)	0.6665 (12)
C(14)	0.0737 (7)	−0.3304 (12)	0.5268 (11)
C(15)	0.1629 (7)	−0.3993 (13)	0.4828 (11)
C(16)	−0.0732 (8)	−0.1300 (14)	0.3639 (13)

[a] Estimated standard deviations are in parentheses.

polarization corrections were applied in all cases. The data was corrected for absorption by using the computer program DIFABS, an empirical method for correcting diffractometer data for absorption effects, written by N. Walker and D. Stuart[13] and adapted by G. Kruger.[14] The absorption correction program was also applied to the crystal structure of $[Re_2(CO)_9(CNBu\text{-}t)]$ (I), which has previously been reported without absorption corrections.[12] Crystal data, details of the data collections, and structural analyses are summarized in Table I.

Table III. Final Atomic Coordinates for $[Re_2(CO)_7(CNMe)_3]$[a,b] (III)

atom	*x/a*	*y/b*	*z/c*
Re(1)	0.3452 (1)	0.3410 (1)	0.2501 (1)
Re(2)	0.1060 (1)	0.4383 (1)	0.2499 (1)
O(1)	0.5907 (10)	0.2467 (10)	0.2489 (13)
O(2)	0.1745 (11)	0.1889 (7)	0.2470 (13)
O(3)	0.4638 (10)	0.5131 (9)	0.2486 (16)
O(5)	−0.1363 (10)	0.5293 (9)	0.2472 (15)
O(6)	0.0208 (13)	0.3164 (9)	0.0446 (12)
O(7)	0.0213 (12)	0.3176 (9)	0.4541 (13)
N(2)	0.2315 (10)	0.5527 (8)	0.4556 (11)
N(3)	0.2327 (10)	0.5564 (9)	0.0433 (11)
N(1)[b]	0.3377 (12)	0.3453 (10)	−0.0470 (13)
N(4)[b]	0.3337 (12)	0.3432 (10)	0.5454 (13)
C(1)	0.4963 (13)	0.2799 (10)	0.2527 (14)
C(2)	0.2392 (12)	0.2469 (10)	0.2478 (14)
C(3)	0.4206 (13)	0.4498 (11)	0.2488 (15)
C(4)	0.3314 (14)	0.3455 (11)	0.4479 (16)
C(5)	−0.0395 (14)	0.4999 (11)	0.2464 (15)
C(6)	0.0511 (13)	0.3627 (10)	0.1234 (14)
C(7)	0.0541 (13)	0.3612 (11)	0.3776 (15)
C(8)	0.3349 (14)	0.3437 (11)	0.0524 (16)
C(9)	0.1844 (10)	0.5138 (8)	0.3808 (11)
C(10)	0.1886 (11)	0.5142 (10)	0.1155 (13)
C(11A)[b]	0.3489 (23)	0.3337 (19)	−0.1779 (25)
C(11B)[b]	0.3455 (23)	0.3299 (19)	0.6754 (25)
C(12)	0.2914 (15)	0.6073 (12)	0.5448 (16)
C(13)	0.2931 (15)	0.6101 (12)	−0.0432 (16)

[a] Estimated deviations in parentheses. [b] Disordered isocyanide: atoms N(1), N(4), C(11A), and C(11B) have site occupancy factors of 0.5; atoms N(1) and N(4), and C(11A) and C(11B), assigned common isotropic temperature factors.

Table IV. Final Atomic Coordinates for $[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$ (IV)[a]

atom	*x/a*	*y/b*	*z/c*
Re	0.1394 (1)	0.2342 (1)	0.6076 (1)
N(1)	0.1248 (11)	0.4887 (16)	0.6599 (6)
N(2)	0.1333 (11)	0.3320 (20)	0.4946 (5)
O(1)	−0.0774 (11)	0.1845 (17)	0.6081 (5)
O(2)	0.1684 (12)	0.1326 (19)	0.7143 (5)
O(3)	0.1819 (13)	−0.0077 (14)	0.5577 (5)
C(1)	−0.0015 (14)	0.2098 (15)	0.6082 (6)
C(2)	0.1549 (13)	0.1637 (17)	0.6758 (7)
C(3)	0.1697 (15)	0.0845 (19)	0.5770 (8)
C(4)	0.1309 (15)	0.3965 (19)	0.6401 (7)
C(5)	0.1371 (13)	0.3024 (16)	0.5366 (7)
C(6)	0.1228 (13)	0.6001 (17)	0.6835 (7)
C(7)	0.1173 (15)	0.6030 (20)	0.7361 (3)
C(8)	0.1178 (18)	0.7201 (23)	0.7582 (10)
C(9)	0.1164 (18)	0.8218 (24)	0.7272 (10)
C(10)	0.1227 (16)	0.8138 (23)	0.6745 (9)
C(11)	0.1246 (14)	0.6984 (19)	0.6526 (7)
C(12)	0.1171 (18)	0.4894 (26)	0.7670 (10)
C(13)	0.1226 (16)	0.6851 (23)	0.5944 (9)
C(14)	0.1327 (14)	0.3626 (18)	0.4427 (7)
C(15)	0.1449 (15)	0.4847 (20)	0.4290 (8)
C(16)	0.1406 (17)	0.5085 (23)	0.3743 (10)
C(17)	0.1342 (17)	0.4100 (24)	0.3427 (10)
C(18)	0.1265 (20)	0.3030 (30)	0.3556 (10)
C(19)	0.1260 (15)	0.2674 (19)	0.4092 (9)
C(20)	0.1540 (18)	0.5888 (23)	0.4682 (10)
C(21)	0.1082 (20)	0.1451 (26)	0.4273 (10)

[a] Estimated standard deviation in parentheses.

The structures were solved and refined by using the program SHELX 82.[15] The metal atoms were placed by a Patterson synthesis, and the positions of the other non-hydrogen atoms were found by difference Fourier synthesis. Refinement of positional parameters of all atoms and anisotropic temperature factors for the non-carbon atoms was done by full-matrix least-squares methods and was considered complete when all parameter shifts were less than 0.5 σ. The scattering factor for Re(0) was taken from ref 16, and anomalous dispersion corrections[17] were made for the rhenium atoms. Final fractional coordinates for all non-hydrogen atoms of the three structures are given in Tables II, III, and IV, respectively. Anisotropic temperature factors for the non-carbon atoms as well as isotropic temperature factors for C atoms are given in the supplementary material. Torsional angles were calculated from the SHELX output of the final atomic coordinates using the program XANADU[18] and are listed in the supplementary material or referred to in the text, where appropriate.

ORTEP[19] drawings of the molecules are shown in Figures 1–4.

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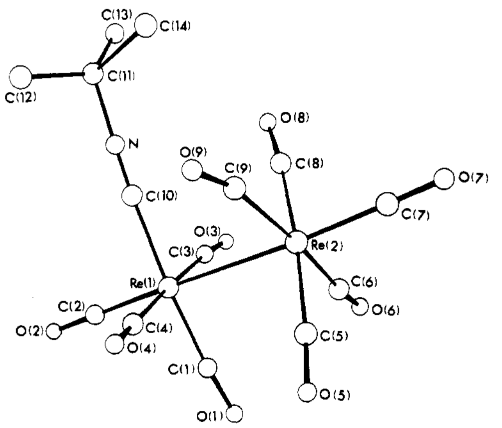

Figure 1. An ORTEP drawing of [$Re_2(CO)_9(CN\text{-}t\text{-}Bu)$].

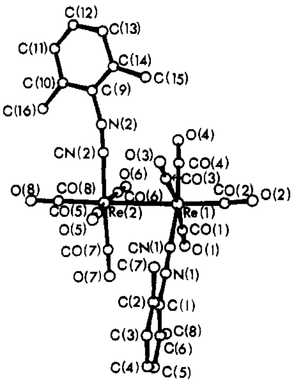

Figure 2. An ORTEP drawing of [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$].

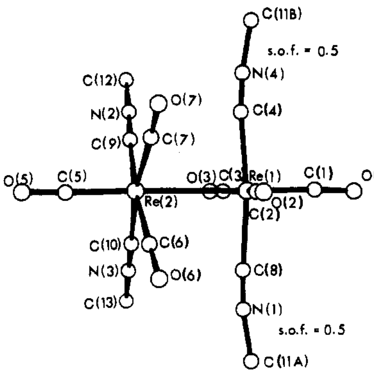

Figure 3. An ORTEP drawing of [$Re_2(CO)_7(CNMe)_3$].

Results

Structure of ($Re_2(CO)_9(CN\text{-}t\text{-}Bu)$] (I). This structure has previously been reported without absorption corrections.[12] The corrected data are contained in the supplementary material. The absorption corrections have modified some of the original bond lengths and bond angle data and the new averaged data are contained in Tables XII–XV. It is to be noted that the new R and R_w values are 5.05% and 3.91% respectively. The basic stereochemical features of the structure have not however changed, and the molecular structure of [$Re_2(CO)_9(CN\text{-}t\text{-}Bu)$] and the numbering system used are shown in Figure 1.

Structure of [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] (II). Compound II was found to crystallize in the centrosymmetric triclinic space group $P\bar{1}$, with $Z = 2$. The molecular structure of [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] and the numbering system used in the crystal structure determination are shown in Figure 2. Bond lengths and bond angles are given in Tables V and VI, respectively.

Table V. Selected Interatomic Distances (Å) for [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] (II)[a]

Re(1)-Re(2)	3.047 (1)		
Re(1)-CO(1)	1.982 (6)	CO(1)-O(1)	1.131 (6)
Re(1)-CO(2)	1.916 (6)	CO(2)-O(2)	1.151 (6)
Re(1)-CO(3)	1.976 (6)	CO(3)-O(3)	1.138 (6)
Re(1)-CO(4)	1.980 (7)	CO(4)-O(4)	1.125 (7)
Re(2)-CO(5)	1.951 (6)	CO(5)-O(5)	1.141 (6)
Re(2)-CO(6)	1.995 (7)	CO(6)-O(6)	1.117 (6)
Re(2)-CO(7)	1.969 (6)	CO(7)-O(7)	1.126 (6)
Re(2)-CO(8)	1.931 (6)	CO(8)-O(8)	1.143 (6)
Re(1)-CN(1)	2.041 (6)	CN(1)-N(1)	1.157 (6)
Re(2)-CN(2)	2.059 (6)	CN(2)-N(2)	1.138 (6)
N(1)-C(1)	1.444 (7)	N(2)-C(9)	1.413 (7)
C(1)-C(2)	1.373 (8)	C(9)-C(10)	1.407 (7)
C(2)-C(3)	1.465 (9)	C(10)-C(11)	1.427 (8)
C(3)-C(4)	1.418 (9)	C(11)-C(12)	1.340 (9)
C(4)-C(5)	1.318 (9)	C(12)-C(13)	1.403 (8)
C(5)-C(6)	1.441 (8)	C(13)-C(14)	1.467 (8)
C(6)-C(1)	1.417 (8)	C(14)-C(9)	1.406 (7)
C(2)-C(7)	1.526 (8)	C(10)-C(16)	1.487 (9)
C(6)-C(8)	1.495 (9)	C(14)-C(15)	1.533 (8)

[a] Estimated standard deviation in parentheses.

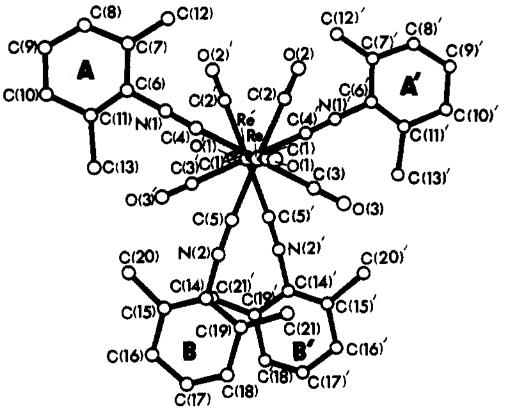

Figure 4. An ORTEP drawing of [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$].

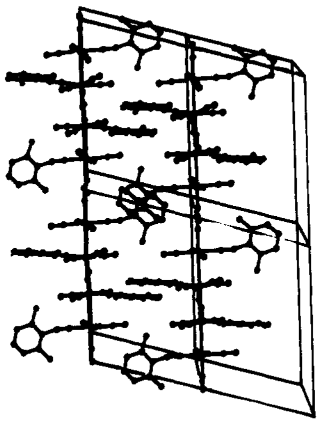

Figure 5. Packing arrangement of [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] molecules viewed down the b axis.

Viewed down the Re–Re bond, the conformation is staggered, as expected. In the crystal, the molecule adopts conformation IIb (Figure 8), with the two isocyanide ligands on different Re atoms. This conformation might be expected to be sterically most favorable, since the bulky 2,6-$Me_2C_6H_3NC$ ligands ("fan-shaped" angles = 106° (wideness) and 53° (thickness)[20]) are as far away from each

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(20) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.

Table VI. Selected Interatomic Angles (deg) for $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ (II)[a]

Re(1)-CO(1)-O(1)	177.8 (6)	C(1)-C(2)-C(3)	117.1 (6)	CO(6)-Re(2)-Re(1)	85.7 (1)
Re(1)-CO(2)-O(2)	175.7 (5)	C(2)-C(3)-C(4)	115.5 (7)	CO(6)-Re(2)-CO(7)	89.4 (2)
Re(1)-CO(3)-O(3)	177.8 (5)	C(3)-C(4)-C(5)	126.7 (8)	CO(6)-Re(2)-CO(8)	95.6 (2)
Re(1)-CO(4)-O(4)	177.8 (5)	C(4)-C(5)-C(6)	119.3 (7)	CO(6)-Re(2)-CN(2)	88.0 (2)
Re(1)-CN(1)-N(1)	178.0 (5)	C(5)-C(6)-C(1)	115.6 (6)	CO(7)-Re(2)-Re(1)	87.9 (1)
CN(1)-N(1)-C(1)	175.9 (5)	N(1)-C(1)-C(2)	115.7 (5)	CO(7)-Re(2)-CO(8)	94.0 (2)
CO(1)-Re(1)-Re(2)	88.0 (2)	N(1)-C(1)-C(6)	118.6 (5)	CO(7)-Re(2)-CN(2)	176.7 (2)
CO(1)-Re(1)-CO(2)	94.0 (2)	C(1)-C(2)-C(7)	124.5 (6)	CO(8)-Re(2)-Re(1)	177.8 (2)
CO(1)-Re(1)-CO(3)	171.1 (2)	C(3)-C(2)-C(7)	118.4 (6)	CO(8)-Re(1)-CN(2)	88.3 (2)
CO(1)-Re(1)-CO(4)	91.0 (2)	C(1)-C(6)-C(8)	119.5 (6)	CN(2)-Re(2)-Re(1)	89.9 (1)
CO(1)-Re(1)-CN(1)	88.1 (2)	C(5)-C(6)-C(8)	124.8 (6)	C(14)-C(9)-C(10)	124.9 (6)
CO(2)-Re(1)-Re(2)	178.0 (2)	Re(2)-CO(5)-O(5)	178.8 (5)	C(9)-C(10)-C(11)	115.3 (6)
CO(2)-Re(1)-CO(3)	94.2 (2)	Re(2)-CO(5)-O(6)	177.6 (5)	C(10)-C(11)-C(12)	121.7 (6)
CO(2)-Re(1)-CO(4)	94.4 (2)	Re(2)-CO(7)-O(7)	179.8 (2)	C(11)-C(12)-C(13)	124.4 (7)
CO(2)-Re(1)-CN(1)	93.8 (2)	Re(2)-CO(8)-O(8)	178.2 (5)	C(12)-C(13)-C(14)	116.5 (6)
CO(3)-Re(1)-Re(2)	83.8 (1)	Re(2)-CN(2)-N(2)	176.8 (5)	C(13)-C(14)-C(9)	117.1 (8)
CO(3)-Re(1)-CO(4)	91.8 (2)	CN(2)-N(2)-C(9)	116.1 (5)	N(2)-C(9)-C(10)	117.3 (5)
CO(3)-Re(1)-CN(1)	87.9 (2)	CO(5)-Re(2)-Re(1)	86.4 (1)	N(2)-C(9)-C(14)	117.8 (5)
CO(4)-Re(1)-Re(2)	85.3 (2)	CO(5)-Re(2)-CO(6)	172.0 (2)	C(9)-C(10)-C(16)	122.2 (6)
CO(4)-Re(1)-CN(1)	171.8 (2)	CO(5)-Re(2)-CO(7)	91.3 (2)	C(11)-C(10)-C(16)	122.5 (6)
CN(1)-Re(1)-Re(2)	86.5 (1)	CO(5)-Re(2)-CO(8)	92.3 (2)	C(9)-C(14)-C(15)	121.7 (5)
C(6)-C(1)-C(2)	125.7 (6)	CO(5)-Re(2)-CN(2)	91.0 (2)	C(13)-C(14)-C(15)	121.2 (5)

[a] Estimated standard deviations in parentheses.

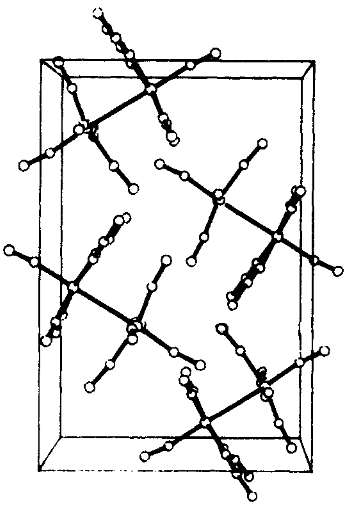

Figure 6. Packing arrangement of $[Re_2(CO)_7(CNMe)_3]$ molecules viewed down the *b* axis.

other as possible, but in the crystal the conformation adopted is probably also determined by crystal packing considerations (see below).

The phenyl rings are essentially planar. The mean planes of the C_6 rings are inclined at 73.1° to each other. This is probably determined mainly by crystal packing forces. As can be seen from the packing diagram (Figure 5) viewed down the *b* axis, the molecules pack in rows, with the orientation of the rings alternating along a row and with the rings lining up in a coplanar manner (less than 2° deviation) with those of the row above.

Structure of $[Re_2(CO)_7(CNMe)_3]$ (III). Complex III crystallizes in the monoclinic space group $P2_1/n$, with $Z = 4$. Unfortunately the structure displayed disorder (see below). Figure 3 shows the molecular structure and the numbering system used in the crystal structure analysis. Bond lengths and bond angles are given in Tables VII and VIII, respectively. The unit cell, viewed down the *b* axis, is shown in Figure 6.

The complex $[Re_2(CO)_7(CNMe)_3]$ might be expected on steric grounds to adopt conformation IIIa (Figure 8), but the structure found in the crystal is IIIc (Figure 8). Again the structure is staggered, with two methyl isocyanide ligands occupying cis-equatorial positions on Re(2), but

Table VII. Selected Interatomic Distances (Å) for $[Re_2(CO)_7(CNMe)_3]$ (III)[a]

Re(1)-Re(2)	3.049 (1)		
Re(1)-C(1)	1.908 (16)	C(1)-O(1)	1.160 (17)
Re(1)-C(2)	1.916 (16)	C(2)-O(2)	1.174 (17)
Re(1)-C(3)	1.937 (18)	C(3)-O(3)	1.126 (19)
Re(2)-C(5)	1.870 (16)	C(5)-O(5)	1.156 (17)
Re(2)-C(6)	1.921 (16)	C(6)-O(6)	1.175 (17)
Re(2)-C(7)	1.936 (17)	C(7)-O(7)	1.139 (18)
Re(2)-C(9)	2.044 (13)	C(9)-N(2)	1.140 (15)
Re(2)-C(10)	2.095 (15)	C(10)-N(3)	1.137 (16)
Re(1)-C(8)	2.121 (17)	C(8)-N(1)	1.066 (19)
Re(1)-C(4)	2.127 (17)	C(4)-N(4)	1.045 (19)
N(1)-C(11A)	1.420 (30)	N(2)-C(12)	1.455 (20)
N(4)-C(11B)	1.414 (29)	N(3)-C(13)	1.431 (20)

[a] Estimated standard deviations in parentheses.

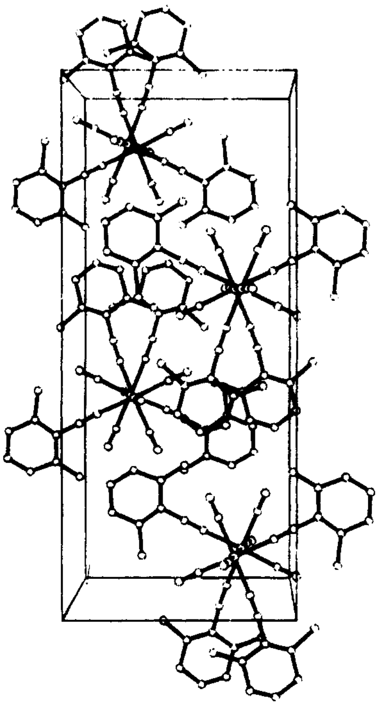

Figure 7. Packing arrangement of $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_4]$ molecules viewed down the *b* axis.

Table VIII. Selected Interatomic Angles (deg) for [$Re_2(CO)_7(CNMe)_3$] (III)[a]

Re(1)-C(1)-O(1)	175.4 (15)	C(2)-Re(1)-C(4)	89.6 (4)	C(5)-Re(2)-Re(1)	178.4 (5)
Re(1)-C(2)-O(2)	179.4 (13)	C(2)-Re(1)-C(8)	88.2 (6)	C(5)-Re(2)-C(6)	93.6 (7)
Re(1)-C(3)-O(3)	179.7 (10)	C(3)-Re(1)-Re(2)	83.6 (4)	C(5)-Re(2)-C(7)	96.3 (7)
Re(1)-C(4)-N(4)	173.0 (16)	C(3)-Re(1)-C(4)	90.5 (7)	C(5)-Re(2)-C(9)	92.8 (6)
Re(1)-C(8)-N(1)	175.1 (15)	C(3)-Re(1)-C(8)	89.9 (7)	C(5)-Re(2)-C(10)	92.2 (6)
C(4)-N(4)-C(11B)	172.2 (22)	C(4)-Re(1)-Re(2)	85.2 (4)	C(6)-Re(2)-Re(1)	86.4 (4)
C(8)-N(1)-C(11A)	170.4 (22)	C(4)-Re(1)-C(8)	171.7 (6)	C(6)-Re(2)-C(7)	89.8 (6)
C(1)-Re(1)-Re(2)	179.2 (5)	C(8)-Re(1)-Re(2)	86.6 (4)	C(6)-Re(2)-C(9)	173.4 (5)
C(1)-Re(1)-C(2)	96.2 (6)	Re(2)-C(5)-O(5)	172.0 (16)	C(6)-Re(2)-C(10)	91.2 (6)
C(1)-Re(1)-C(3)	96.5 (6)	Re(2)-C(6)-O(6)	178.1 (14)	C(7)-Re(2)-Re(1)	85.3 (4)
C(1)-Re(1)-C(4)	93.9 (6)	Re(2)-C(7)-O(7)	178.0 (15)	C(7)-Re(2)-C(9)	91.2 (6)
C(1)-Re(1)-C(8)	94.2 (6)	Re(2)-C(9)-N(2)	176.7 (12)	C(7)-Re(2)-C(10)	171.4 (6)
C(2)-Re(1)-Re(2)	83.7 (4)	Re(2)-C(10)-N(3)	179.0 (14)	C(9)-Re(2)-Re(1)	87.2 (3)
C(2)-Re(1)-C(3)	167.2 (6)	C(9)-N(2)-C(12)	175.9 (15)	C(9)-Re(2)-C(10)	86.7 (5)
		C(10)-N(3)-C(13)	177.1 (14)	C(10)-Re(2)-Re(1)	86.3 (4)

[a] Estimated standard deviations in parentheses.

Table IX. Selected Interatomic Distances (Å) for [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$] (IV)[a]

Re(x,y,z)-Re($^1/_2 - x, ^1/_2 - y, z$): 3.081 (2)

Re-C(1)	1.968 (20)	C(1)-O(1)	1.088 (21)
Re-C(2)	1.980 (20)	C(2)-O(2)	1.093 (21)
Re-C(3)	1.924 (21)	C(3)-O(3)	1.174 (23)
Re-C(4)	2.031 (22)	C(4)-N(1)	1.171 (25)
Re-C(5)	2.027 (18)	C(5)-N(2)	1.161 (22)
N(1)-C(6)	1.407 (24)	N(2)-C(14)	1.413 (22)
C(6)-C(7)	1.391 (26)	C(14)-C(15)	1.438 (29)
C(7)-C(8)	1.448 (32)	C(15)-C(16)	1.472 (30)
C(8)-C(9)	1.413 (35)	C(16)-C(17)	1.395 (34)
C(9)-C(10)	1.396 (31)	C(17)-C(18)	1.263 (37)
C(10)-C(11)	1.428 (32)	C(18)-C(19)	1.472 (35)
C(11)-C(6)	1.381 (27)	C(19)-C(14)	1.396 (28)
C(7)-C(12)	1.524 (33)	C(15)-C(20)	1.573 (32)
C(11)-C(13)	1.545 (28)	C(19)-C(21)	1.485 (34)

[a] Estimated standard deviations in parentheses.

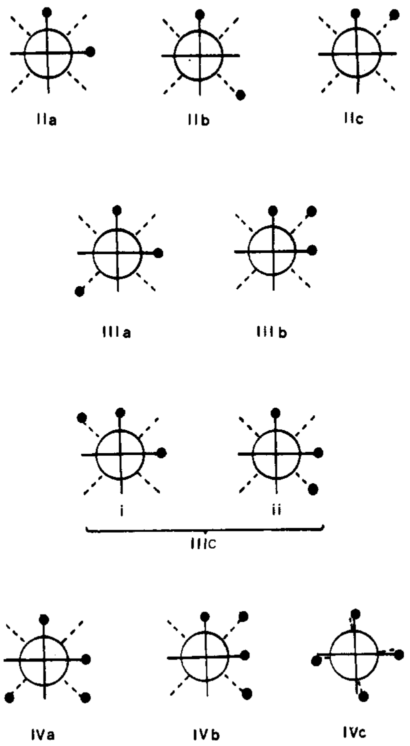

Figure 8. Possible Newman projections of the [$Re_2(CO)_{10-n}(CNR)_n$] (n = 2–4) complexes viewed down the Re–Re bond axis. [Complex I (not shown) corresponds to the monosubstituted derivative, and if equatorial substitution only is considered, then only one staggered conformer is possible.]

the third MeNC ligand on Re(1) is disordered with respect to the carbonyl trans to it, with 50% occupancy of both sites, which are equivalent with respect to the two isocyanide ligands on Re(2) (Figure 8 (IIIc) i and ii). Disordered N and O atoms are superimposed in this description. Disorder of this type has been observed previously with MeNC ligands[21] and is thought to be due to the relatively small size of the MeNC ligand ("fan-shaped" angle[20] for MeNC = 52° (wideness) and 52° (thickness)) and its electronic similarity to CO.[21] The distance C(11A)–C(11B) between the methyl atom C(11A) and the methyl atom C(11B) of a neighboring molecule (translated by (001)) is within bonding distance (1.57 (4) Å). However, the atoms C(11A) and C(11B) constitute the disordered methyl isocyanide group, with site occupancy factors (sof) of 0.5.

Structure of [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$] (IV). Compound IV crystallizes in the orthorhombic space group *Pbcn* with Z = 4, the asymmetric unit being an Re($CO)_3(CNC_6H_3Me_2\text{-}2,6)_2$ fragment, the two halves of the molecule being related by the symmetry operator ($x - ^1/_2$, $y - ^1/_2$, z). The molecular structure and the numbering system used in the crystal structure analysis are shown in Figure 4. Bond lengths and bond angles are given in Tables IX and X, respectively.

From steric considerations of the RCN ligand, the [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$] molecule might have been expected to adopt the eclipsed conformation IVc (Figure 8). Of the possible staggered conformations IVa and IVb (Figure 8), IVb would be less favorable on steric grounds. The molecular geometry found in the crystal is that of IVa with cis-equatorial substitution of a pair of isocyanide ligands on each Re atom.

The relative arrangements of the xylyl (xylyl = 2,6-$Me_2C_6H_3$) isocyanide ligands adopted (see above), as well as the relative orientation of the xylyl rings, probably reflect both steric requirements and crystal packing forces. The C_6 rings are essentially planar. The xylyl rings are all close to being coplanar, the angles between the mean planes through rings A and B (A′ and B′), A and B′ (A′ and B), A and A′, and B and B′, being 6.6, 5.7, 4.8, and 2.4°, respectively. Figure 7 shows the packing of the molecules in the unit cell, viewed down the b axis. The xylyl rings of one molecule fit neatly into the gaps between the xylyl rings of adjacent molecules.

Discussion

Product Stereochemistry. The structure of the unsubstituted dimer [$Re_2(CO)_{10}$][4] provides a starting point

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(21) Prasad, P. N. *Spectrochim. Acta, Part A* 1977, *33A*, 335.

Table X. Selected Interatomic Angles (deg) for $[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$ (IV)[a]

Re-C(1)-O(1)	172.8 (19)	C(9)-C(10)-C(11)	117.6 (23)	C(4)-Re-C(5)	92.6 (7)
Re-C(2)-O(2)	174.0 (19)	C(10)-C(11)-C(6)	119.9 (18)	C(2)-Re-C(5)	174.5 (7)
Re-C(3)-O(3)	175.7 (20)	C(12)-C(7)-C(6)	120.9 (20)	C(3)-Re-C(4)	170.7 (8)
Re-C(4)-N(1)	178.1 (18)	C(12)-C(7)-C(8)	123.9 (20)	C(1)-Re-Re'[a]	178.5 (6)
Re-C(5)-N(2)	174.2 (18)	C(13)-C(11)-C(6)	120.6 (19)	C(19)-C(14)-C(15)	126.3 (19)
C(4)-N(1)-C(6)	177.0 (20)	C(13)-C(11)-C(10)	119.5 (19)	C(14)-C(15)-C(16)	114.6 (19)
C(5)-N(2)-C(14)	176.6 (22)	N(1)-C(6)-C(7)	117.7 (18)	C(15)-C(16)-C(17)	116.3 (23)
C(2)-Re-Re'[b]	86.6 (8)	N(1)-C(6)-C(11)	117.5 (17)	C(16)-C(17)-C(18)	127.6 (28)
C(3)-Re-Re'[b]	83.5 (8)	C(1)-Re-C(2)	92.5 (7)	C(17)-C(18)-C(19)	121.5 (27)
C(4)-Re-Re'[b]	87.3 (8)	C(1)-Re-C(3)	95.5 (8)	C(18)-C(19)-C(14)	113.4 (21)
C(5)-Re-Re'[b]	88.4 (8)	C(1)-Re-C(4)	93.8 (8)	C(20)-C(15)-C(14)	124.4 (19)
C(11)-C(6)-C(7)	124.8 (18)	C(1)-Re-C(5)	92.6 (7)	C(20)-C(15)-C(16)	120.8 (20)
C(6)-C(7)-C(8)	115.1 (20)	C(2)-Re-C(3)	90.2 (8)	C(21)-C(19)-C(14)	121.8 (21)
C(7)-C(8)-C(9)	120.7 (23)	C(2)-Re-C(4)	89.3 (8)	C(21)-C(19)-C(18)	124.5 (23)
C(8)-C(9)-C(10)	121.6 (25)	C(3)-Re-C(5)	87.2 (8)	N(2)-C(14)-C(15)	118.5 (19)
				N(2)-C(14)-C(19)	115.1 (19)

[a] Estimated standard deviation in parentheses. [b] Re' is related to Re by the symmetry operator ($^1/_2 - x$, $^1/_2 - y$, z).

Table XI. Metal-Metal Bond Length Data for the Complexes $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0-4)

complex	Re-Re, Å
$[Re_2(CO)_{10}]$	3.041 (1)[a]
$[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$	3.048 (1)
$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$	3.047 (1)
$[Re_2(CO)_7(CNMe)_3]$	3.049 (1)
$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$	3.081 (2)

[a] Reference 4.

for discussing the isocyanide-substituted derivatives. $[Re_2(CO)_{10}]$ adopts a staggered conformation in which the M-CO_{ax} bond length is shorter than the M-CO_{eq} bond length. The variation in M-CO bond lengths is ascribed to competition for d electrons between pairs of mutually trans CO ligands. Consequently on electronic grounds isocyanide substitution would be predicted to be equatorial rather than axial. However, steric effects may dominate, as has been observed for bulky ligands, e.g., PMe_2Ph (Tolman cone angle 122°[22])in ax-$[Mn_2(CO)_9(PMe_2Ph)]$.[23] Equatorial substitution is indeed observed for the sterically undemanding t-BuNC ligand in $[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$ (Figure 1).

Disubstitution of $[Re_2(CO)_{10}]$ can potentially lead to a wide range of structures, but providing electronic rather than steric factors dominate, diequatorial substitution is predicted. Even here two possibilities exist (Figure 8 (II)), and the $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ complex is observed to have the two isocyanide ligands attached to *different* atoms and to adopt the sterically most probable conformation IIb. In this conformation the ligands are as far away from each other as possible (structure IIa (Figure 8) has been observed for an isomer of $[Mn_2(CO)_8(CN\text{-}t\text{-}Bu)_2]$[24]).

Several structures are also possible for the trisubstituted derivatives, but if the isocyanide ligand is restricted to cis position on steric and electronic grounds, the most likely structure is that indicated in Figure 8 (III). This geometry is indeed observed for $[Re_2(CO)_7(CNMe)_3]$, but unexpectedly conformer IIIc (and not IIIa) is observed. This could relate to the disorder observed in the structure which places the lone MeNC ligand in coordination sites shown in Figure 8 (IIIc) i and ii.

$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$ could be expected to adopt any of the conformations, IVa–c shown in Figure 8, if equatorial substitution again occurs. The conformer observed is IVa which is expected on steric grounds.

Thus from a comprehensive investigation of the structures of $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 1–4) it is apparent that if steric factors are minimized, the ligands always occupy the electronically favored cis positions. Thus, factors responsible for substitution of monometallic complexes apply equally well to metal dimers and presumably to larger metal clusters.[25]

We have carried out a literature survey of all known dimeric structures containing two Re–Re atoms in bonding interaction. Although a wide range of complexes with bridging ligands have been characterized by X-ray crystallography, only five structures with no bridging ligands have been determined. The three monosubstituted carbene complexes $[Re_2(CO)_9(carbene)]$ (carbene = CH(OMe),[26] $C(OMe)[Si(C_6H_5)_3]$,[27] and $C(OEt)[Si(C_6H_5)_3]$[27,28] all occupy the electronically favorable equatorial sites. However the disubstituted products $[Re_2(CO)_8\{C(OEt)[Si(C_6H_5)_3]\}]$[27] and $[Re_2(CO)_8(PMe_2Ph)_2]$[29] have axial–equatorial and axial–axial ligand stereochemistry, respectively, indicating that steric effects have become significant.

Structural Trends. One of the major objectives of the crystal structure determinations was to obtain bond parameter data and to ascertain the effect of isocyanide substitution on these parameters.

(1) Re–Re Bond Length. Since isonitriles are weaker π-acceptors (and better σ-donors) than CO ligands,[30] increasing RNC substitution could be expected to result in a weakening and hence a lengthening of the metal–metal bond.[20] The collected bond length data for the $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0–4) series (Table XI) indicates that there is only a slight increase in the bond length when n = 4 and a negligible increase for $n < 4$. The inference is that the isocyanide ligands are (electronically) hardly affecting the strength of the Re–Re bond as reflected by bond length criteria. A lengthening of the Re–Re bond due to steric effects could also be important, but it is clear that effects must be minimal since Re–Re–C_{eq} angles are

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Table XII. Average M–C Bond Length Data for the Complexes [$Re_2(CO)_{10-n}(CNR)_n$] (n = 0–4)

	av Re–C, Å			
		Re–CO_{eq}		
complex	Re–CO_{ax}	trans to CO	trans to CN	Re–CN
[$Re_2(CO)_{10}$][a]	1.929 (7)	1.987 (6)		
[$Re_2(CO)_9$(CN-*t*-Bu)]	1.902 (19)	1.983 (20)	1.916 (18)	2.068 (15)
[$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$]	1.924 (6)	1.976 (6)	1.975 (7)	2.050 (6)
[$Re_2(CO)_7(CNMe)_3$][b]	1.889 (16)	1.927 (16)	1.929 (17)	2.070 (14) 2.124 (17)[c]
[$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$]	1.968 (20)		1.952 (20)	2.029 (20)

[a] Reference 4. [b] Disordered structure. [c] Average for disordered MeNC ligand.

Table XIII. Average M–M–C Bond Angle Data (deg) for the Complexes [$Re_2(CO)_{10-n}(CNR)_n$] (n = 0–4)

complex	M–M–CO_{ax}	M–M–CO_{eq}	M–M–CN
[$Re_2(CO)_{10}$][a]	176.3 (2)	86.4 (2)	
[$Re_2(CO)_9$(CN-*t*-Bu)]	177.0 (6)	86.8 (5)	87.5 (4)
[$Re_2(CO)_8$-($CNC_6H_3Me_2$-2,6)$_2$]	177.9 (2)	86.2 (1)	88.2 (1)
[$Re_2(CO)_7(CNMe)_3$][b]	178.8 (5)	84.8 (4)	86.3 (4)
[$Re_2(CO)_6$-($CNC_6H_3Me_2$-2,6)$_4$]	178.5 (8)	85.1 (8)	87.9 (8)

[a] Reference 4. [b] Disordered structure.

acute (see below) and the Re–Re bond length remains relatively constant. Steric effects could, however, be responsible for the Re–Re bond lengthening observed for [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$].

(2) Re–CO Bond Lengths. It has been reported that M–CO_{ax} bonds are shorter than M–CO_{eq} bonds, implying stronger bonding of axial carbonyls to the metal. However, when considering the substituted isocyanide derivatives, the possible effect of the isocyanide ligand on the trans carbonyl could also be important.[30] Since the isocyanide ligand is a poorer π-acceptor than carbonyl,[31] it would be expected that the M–CO bond trans to an RNC ligand would be shorter than that trans to another CO.[32]

Although this effect is indeed observed for [$Re_2(CO)_9$(CN-*t*-Bu)], with Re–C(1) trans to CN-*t*-Bu (1.916 (8) Å) shorter than the average value of the other Re–CO_{eq} bonds (average 1.938 (2) Å), this trend does not continue for the [$Re_2(CO)_{10-n}(CNR)_n$] (n = 2–4) derivatives (see Table XII). However, for the [$Re_2(CO)_{10-n}(CNR)_n$] (n = 1–3) complexes, the average Re–CO_{ax} bond is significantly shorter than the average Re–CO_{eq} (trans to CO or CN) bonds, as expected (see above).

(3) Molecular Conformation. In all the structures discussed (I–VI), the molecule adopts a staggered conformation, like the parent carbonyl [$Re_2(CO)_{10}$],[4] with C–M–M–C torsional angles close to the ideal 45°. (Torsional angles of structures I–VI are listed in the supplementary material). A staggered conformation is expected to minimize repulsions between equatorial ligands.[33] The C_{ax}–M–M–C_{ax} fragment is essentially linear, as indicated by M–M–CO_{ax} bond angles of ca. 177° (see Table XIII).

(4) C–M–C and M–M–C_{eq} Bond Angles. In structures I–VI, all the C–M–C angles are close to 90°, but significantly, the C_{ax}–M–C_{eq} angles are all greater than 90°, while the C_{eq}–M–C_{eq} angles are ca. 90°. (See Table XIV). This is true whether the equatorial ligand is a carbonyl or isocyanide ligand. Hence the ligands are all bending slightly inwards toward the M–M bond. This is also reflected in the acute M–M–C_{eq} angles (ca. 86°) (see Table XIII). Similar trends were observed for [$M_2(CO)_{10}$] (M = Re, Mn).[3,4]

This is throught to be a genuine electronic effect and has been rationalized by Elian and Hoffman[34] on the basis of molecular orbital theory. From a consideration of energy level diagrams, theoretical predictions indicate that the energetically most favorable geometry corresponds to an C_{eq}–M–C_{ax} angle of slightly greater than 90°, at which point π interaction is maximized and antibonding interaction minimized.

The consistency of the C_{ax}–M–C_{eq} (93–96°), C_{eq}–M–C_{eq} (ca. 90°), and M–M–C_{eq} (85–88°) bond angles for the series [$M_2(CO)_{10-n}(CNR)_n$] (M = Re, n = 0–4; see Table XIII and XIV) indicate that this effect is genuine. Also significant is the observation that the M–M–CN angle is less than 90° for these structures (Table XIII).

(5) M–C–O, M–C–N, and C–N–C Bond Angles. In all the structures I–IV both the carbonyl and the isocyanide ligands coordinate in an essentially linear fashion, with M–C–O and M–C–N bond angles all in the range 170–179° (see Table XV). *Near* linearity of M–C–R bonds for $M(CR)_n$ (R = O, N; $n > 1$) groups has been predicted on electronic grounds.[35]

The observation that deviations from linearity are not greater for the M–C–N bonds than for the M–C–O bonds (see Table XV), nor indeed do more highly substituted complexes show any greater distortions, is indicative of the apparent lack of any noticeable effect of the steric bulk[14] of the isocyanide ligands on the molecular geometry.

Further, the isocyanide ligands themselves show only small deviations from linearity, the C–N–C angles being generally in the range 170–180° (see Table XV). This slight deviation from linearity is normal for terminal isocyanide ligands (isocyanides with C–N–C angles >170° are considered to be essentially linear[36]). Individual isocyanide ligands which show slight deviations from linearity (e.g., II, CN(2)–N(2)–C(9) = 166.1 (5)°; III, C(8)–N(1)–C(11A) = 170.4 (22)°) probably reflect the influence of crystal packing forces. A greater bending of the isocyanide ligands in the more highly substituted complexes is not observed.

(6) Packing. The role of crystal packing forces in determining structure should not be neglected. In the case of [$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$] (II) and [$Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4$] (IV), the conformation adopted in the crystal as well as the relative orientation of the xylyl rings, is probably determined largely by the influence of packing forces. (See packing diagrams of II, III, and IV, Figures 5, 6, and 7, respectively.) For the trisubstituted [Re_2-

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Table XIV. Average Cis C-M-C Bond Angle Data (deg) for the Complexes $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0-4)

complex	CO_{ax}-M-CO_{eq}	CO_{ax}-M-CN	CO_{eq}-M-CO_{eq}	CO_{eq}-M-CN	CN-M-CN
$[Re_2(CO)_{10}]^a$	93.7 (3)		89.8 (2)		
$[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$	93.3 (8)	92.1 (6)	89.8 (8)	89.9 (7)	
$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$	94.1 (2)	91.1 (2)	90.9 (2)	88.8 (2)	
$[Re_2(CO)_7(CNMe)_3]^b$	95.7 (7)	93.3 (6)	89.8 (6)	90.1 (6)	86.7 (5)
$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$	94.0 (8)	93.2 (8)	90.2 (8)	88.3 (8)	92.6 (7)

[a] Reference 4. [b] Disordered structure.

Table XV. Average Bond Data (deg) for the M-C-O, M-C-N, and C-N-C Bond Angles of the Complexes $[Re_2(CO)_{10-n}(CNR)_n]$ (n = 0-4)

complex	M-C-O_{ax}	M-C-O_{eq}	M-C-N	C-N-C
$[Re_2(CO)_{10}]^a$	177.5 (7)	178.0 (5)		
$[Re_2(CO)_9(CN\text{-}t\text{-}Bu)]$	177.0 (17)	175.9 (17)	175.5 (13)	175.7 (18)
$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$	177.0 (5)	178.3 (5)	177.4 (5)	171.0 (5)
$[Re_2(CO)_7(CNMe)_3]^b$	173.7 (16)	178.8 (13)	177.9 (13) 174.1 (14)^c	176.5 (15) 171.3 (22)^c
$[Re_2(CO)_6(CNC_6H_3Me_2\text{-}2,6)_4]$	172.8 (9)	174.9 (20)	176.2 (18)	176.8 (21)

[a] Reference 4. [b] Disordered structure. [c] Average for disordered MeNC ligand.

$(CO)_7(CNMe)_3]$, the conformation adopted in the crystal IIIc (Figures 6 and 8) is probably favored over the other possible conformations IIIa and IIIb (Figure 8) due to packing considerations. In solution all isomers probably coexist.

It has been claimed[37] that packing forces could also be responsible for small deviations in geometry. For example, nonbonded O···O interactions could result in M–C–O bonds deviating from linearity by 5–10°.

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Supplementary Material Available: Tables of bond lengths, bond angles, and final atomic coordinates for I, isotropic temperature factors for the carbon atoms and anisotropic temperature factors for the non-carbon atoms of I–IV, torsion angles for $[Re_2(CO)_{10-n}(CNR)_n]$, and structure factor amplitudes for I–IV (69 pages). Ordering information is given on any current masthead page.

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Aminobenzenes. 18.[1a] Crystal and Molecular Structures of Novel (Arene)chromium Tricarbonyl Complexes

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Several new (1,3,5-tris(dialkylamino)benzene)chromium tricarbonyl (chromium tricarbonyl = TCC) complexes (**2**) were prepared and crystal structures for two of them, **2a** ((1,3,5-tripyrrolidinobenzene)TCC) and **2b** ((1,3,5-tripyrrolidino-2-methylbenzene)TCC), were determined to high precision with X-ray data collected from cooled crystals ($T \approx 120$ K). Complex **2a** crystallizes in space group symmetry $P\bar{1}$ with a = 8.7670 (5) Å, b = 10.6023 (8) Å, c = 11.6337 (8) Å, α = 66.724 (6)°, β = 72.560 (6)°, γ = 79.651 (7)°, and Z = 2. For **2b** the space group is $P2_1/c$ with a = 12.323 (1) Å, b = 8.2651 (8) Å, c = 23.902 (2) Å, β = 123.114 (7)°, and Z = 4. The model for **2a** was refined with 13110 contributing reflections to give R_w = 0.053; for **2b** refinement with 9154 reflections gave R_w = 0.058. A crystal structure was also determined for the [(phenyl(trimethylsiloxy)methyl)benzene]TCC complex (**3**) for which the space groups is $P2_1/c$ with a = 6.282 (1) Å, b = 11.319 (4) Å, c = 26.962 (12) Å, β = 93.82 (2)°, and Z = 4 (room temperature). All three complexes display a close approximation to the syn-e conformation for the (arene)TCC moiety. The rotational barriers for compounds **2** could not be established because of their low solubility. The application of conclusions from crystal structures to reaction behavior in solution was proved in the case of the [(phenyl)trimethylsiloxy)methyl)benzene]TCC complex (**3**). The experimental results are in agreement with the reactivity pattern calculated for the crystal structure determined for **3**.

Introduction

The conformation of the chromium tricarbonyl (TCC) group in (arene)TCC complexes has a decisive influence on the reactivity of these compounds; e.g., there is a remarkable regioselectivity in their reactions with electrophiles[2] as well as with nucleophiles.[3] From calculations,

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