Is the Metal–Metal Bond Length in $MnRe(CO)_{10}$ Anomalous? X-ray Crystal Structure Determination of $MnRe(CO)_9L$ (L = $^{t}BuNC$, $P(CH_2C_6H_5)_3$) and $MnRe(CO)_8(CNBu^t)(PPh_3)$

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The crystal structure determinations of $MnRe(CO)_9(CNBu^t)$ (**1**), $MnRe(CO)_9P(CH_2C_6H_5)_3$ (**2**), and $MnRe(CO)_8(CNBu^t)(PPh_3)$ (**3**) have been performed. Crystal data: (**1**) monoclinic, $P2_1/n$, $a = 12.030$ (7) Å, $b = 20.834$ (8) Å, $c = 15.22$ (1) Å, $\beta = 91.683$ (6)°, $Z = 8$, and $R = 0.075$; (**2**) triclinic, $P\bar{1}$, $a = 12.314$ (7) Å, $b = 14.305$ (7) Å, $c = 19.198$ (6) Å, $\alpha = 68.40$ (5)°, $\beta = 78.390$ (4)°, $\gamma = 88.98$ (4)°, $Z = 4$, and $R = 0.050$; (**3**) monoclinic, $P2_1/c$, $a = 17.841$ (3) Å, $b = 9.616$ (2) Å, $c = 20.505$ (4) Å, $\beta = 113.15$ (1)°, $Z = 4$, and $R = 0.037$. In all three structures d_{Mn-Re} is found to be 2.963 (±7) Å, suggesting that the site and degree of substitution on $MnRe(CO)_{10}$ have little influence on the bond length value. The value lies midway between the metal–metal bond lengths of $Mn_2(CO)_{10}$ (d_{Mn-Mn} = 2.904 (1) Å) and $Re_2(CO)_{10}$ (d_{Re-Re} = 3.041 (1) Å).

Introduction

Some years ago, while investigating the PdO-catalyzed synthesis of $MnRe(CO)_9L$ (L = isocyanide) from $MnRe(CO)_{10}$ and L, we performed an X-ray crystal structure determination of $MnRe(CO)_9(CNBu^t)$.[1] Although the data were of poor quality and never published, we were able to definitively establish that substitution had occurred at the Re atom in an equatorial site. Further, the Mn–Re bond length appeared "normal" at 2.96 Å. Viz., the following data can be presented: (i) The value lay halfway between the reported metal–metal bond lengths for $Mn_2(CO)_{10}$[2] (d_{Mn-Mn} = 2.9038 (6),[3] 2.895 (1) Å[4]) and $Re_2(CO)_{10}$ (d_{Re-Re} = 3.0413 Å[3]). (ii) An X-ray structure determination reported by Struchkov and co-workers on $MnRe(CO)_{10}$ in 1967 gave d_{Mn-Re} = 2.96 Å.[5] (iii) X-ray structural data for related substituted Mn–Re-substituted complexes known at that time also gave d_{Mn-Re} values close to 2.96 Å ($[Re(CO)_5H]Re(CO)_4Mn(CO)_5$, 2.960 (3) Å;[6] $Mn(CO)_5Re(CO)_4[C(OMe)CH_3]$, 2.972 (1) Å[7]).

However, in 1986 the X-ray structure of $MnRe(CO)_{10}$ was redetermined[8] in a corrected space group ($I2/a$ instead of I_a[5]) and the authors reported a shorter d_{Mn-Re} bond length of 2.909 (1) Å, a value nearly identical with d_{Mn-Mn} in $Mn_2(CO)_{10}$. This redetermined value suggests that the bond lengths of heteronuclear dimers may not be related in any intuitive way to the bond lengths of the related homonuclear dimers. Since the data "could reasonably serve as a reference structure for other Mn–Re bonded dissociation energies for $M_2(CO)_{10}$ (M_2 = Mn_2, Re_2, MnRe)[8,9] complexes", it is clear that the bond length data have implications far beyond the actual measurement.

In recent years we have been synthesizing and studying a range of substituted metal dimer carbonyl complexes and have carried out a range of crystal structure determinations on the new complexes to assist with the product characterization.[10] From these studies we have consistently noted that the metal–metal bond lengths of the heteronuclear dimers can be related to the bond lengths of the related homonuclear dimers (see below). We have thus determined the crystal structures of a series of Mn–Re complexes to obtain further information on the Mn–Re bond length. In particular, we have carried out crystal structure determinations on an axial ($MnRe(CO)_9P(CH_2C_6H_5)_3$), an equatorial ($MnRe(CO)_9(CNBu^t)$), and a disubstituted ($MnRe(CO)_8(CNBu^t)(PPh_3)$) complex to assess the influence of the different electronic/steric effects of the substituents on the Mn–Re bond length. Our data have also been compared to that for the structure of $Re(CO)_5Mn(CO)_3(^{i}PrDAB)$ (DAB = 1,4-diaza-1,3-butadiene).[11]

Table I. Crystallographic Data for **1–3**

chem form	$MnReC_{14}H_9NO_9$	$MnReC_{30}H_{21}O_9P$	$MnReC_{31}H_{24}NO_8P$
fw	576.37	797.59	810.63
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	12.030 (7)	12.314 (7)	17.841 (3)
b, Å	20.834 (8)	14.305 (7)	9.616 (2)
c, Å	15.22 (1)	19.198 (6)	20.505 (4)
V, Å^3	3813 (8)	3074 (3)	3234 (1)
α, deg		68.40 (5)	
β, deg	91.683 (6)	78.390 (4)	113.15 (1)
γ, deg		88.98 (4)	
Z	8	4	4
d_{calc}, g cm^{-3}	1.965	1.724	1.664
T, °C	23 ± 2	23 ± 2	23 ± 2
2θ range, deg	3–65	3–23	3–27
no. of data colld	6658	7203	8416
no. of data refined	5247	5169	4924
no. of variables	236	213	398
R^a	0.075	0.050	0.037
$R_w{}^b$	0.072	0.045	0.031

[a] $R = \sum|F_o - F_c|/\sum F_o$. [b] $R = \sum(|F_o - F_c|w^{1/2})/\sum(F_o w^{1/2})$.

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for **1**

	x/a	*y/b*	*z/c*	$U_{eq}{}^a$		*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
MnA	3063 (2)	−3452 (1)	1268 (2)	37 (1)	MnB	1280 (2)	−3520 (1)	6984 (2)	29 (1)
ReA	1895 (1)	−4252 (0)	2557 (1)	31 (0)	ReB	3703 (1)	−3778 (0)	6947 (1)	32 (0)
O1A	4229 (16)	−2670 (9)	−19 (14)	106 (6)	O1B	−1157 (11)	−3393 (7)	6909 (12)	74 (5)
O2A	4264 (14)	−2956 (8)	2862 (12)	81 (5)	O2B	1681 (14)	−2931 (7)	8734 (10)	69 (5)
O4A	1565 (12)	−4137 (7)	−17 (11)	65 (4)	O3B	1272 (14)	−4130 (8)	5206 (10)	71 (5)
O3A	4697 (13)	−4544 (8)	1248 (15)	113 (7)	O4B	1189 (11)	−4793 (6)	7904 (10)	61 (4)
O5A	1277 (12)	−2472 (7)	1471 (13)	94 (6)	O5B	1790 (14)	−2270 (7)	6125 (12)	88 (5)
O7A	1548 (15)	−3057 (7)	3743 (11)	83 (5)	O6B	4101 (12)	−2410 (8)	7720 (10)	76 (5)*
O6A	4162 (13)	−4521 (8)	3495 (13)	89 (6)	O7B	3619 (13)	−4287 (8)	8837 (11)	71 (5)
O8A	−282 (11)	−3894 (7)	1590 (10)	62 (4)	O8B	3683 (14)	−3287 (9)	5035 (11)	91 (6)
O10A	727 (13)	−5138 (7)	3837 (10)	64 (4)	O9B	6182 (10)	−4037 (6)	6885 (9)	52 (4)
N1A	2236 (12)	−5458 (7)	1276 (10)	40 (4)	N1B	3076 (12)	−5213 (8)	6296 (10)	41 (4)*
C1A	3763 (18)	−2976 (10)	468 (17)	64 (6)	C1B	−190 (15)	−3440 (8)	6968 (13)	38 (5)
C2A	3799 (15)	−3147 (9)	2216 (17)	52 (6)	C2B	1545 (15)	−3154 (8)	8046 (14)	40 (5)
C4A	2149 (16)	−3872 (10)	476 (15)	49 (6)	C3B	1298 (16)	−3895 (9)	5913 (15)	46 (5)
C3A	4076 (17)	−4116 (13)	1254 (17)	68 (7)	C4B	1245 (15)	−4304 (9)	7532 (14)	45 (5)
C5A	1949 (17)	−2854 (10)	1392 (15)	53 (6)	C5B	1617 (15)	−2745 (10)	6459 (15)	50 (5)
C7A	1660 (16)	−3485 (12)	3342 (12)	54 (6)	C6B	3980 (18)	−2900 (10)	7407 (19)	88 (8)
C6A	3341 (16)	−4425 (8)	3109 (17)	63 (6)	C7B	3644 (16)	−4097 (9)	8122 (14)	44 (5)
C8A	551 (14)	−4056 (9)	1973 (16)	55 (6)	C8B	3654 (17)	−3486 (11)	5723 (15)	57 (6)
C10A	1151 (15)	−4804 (9)	3376 (12)	35 (4)	C9B	5220 (13)	−3914 (8)	6910 (10)	25 (4)
C9A	2126 (14)	−5040 (9)	1691 (12)	36 (5)	C10B	3294 (15)	−4718 (11)	6520 (17)	72 (7)
C11A	2381 (16)	−5991 (9)	636 (15)	49 (5)	C11B	2743 (16)	−5876 (9)	6082 (17)	56 (6)
C12A	1317 (22)	−6380 (14)	624 (22)	134 (12)	C12B	1475 (17)	−5880 (11)	5907 (20)	94 (9)
C13A	3334 (22)	−6378 (12)	1000 (20)	111 (10)	C13B	3372 (26)	−6054 (13)	5275 (20)	132 (11)
C14A	2587 (27)	−5711 (11)	−238 (15)	108 (11)	C14B	3043 (25)	−6239 (10)	6979 (19)	110 (10)

[a] Asterisks indicate isotropic temperature factors. $U_{eq} = {}^1/_3\sum_{i=1}^3\sum_{j=1}^3 u_{ij}a_i^*a_j^*(a_ia_j)$.

Experimental Section

$Mn_2(CO)_{10}$ was purchased from Strem Chemicals, and the PdO catalysts were purchased from Johnson-Matthey Chemicals. $MnRe(CO)_{10}$ was synthesized from $Na[Mn(CO)_5]$ and $Re(CO)_5(CF_3SO_3)$ as described previously,[12] and its purity was confirmed by IR spectroscopy. ^tBuNC, PPh_3, and $P(CH_2C_6H_5)_3$ were used without any additional purification. Me_3NO was dried by azeotropic distillation in toluene prior to use. All reactions were performed under nitrogen in the dark using foil-wrapped flasks. Solvents were routinely dried and distilled.

IR spectra were recorded on a Jasco 500 FT spectrometer, and NMR spectra, on a Brucker AC 200 NMR spectrometer (C_6D_6; ^1H relative to TMS; ^{31}P relative to H_3PO_4).

Synthesis of $(CO)_5MnRe(CO)_4(CNBu^t)^1$ (1). $MnRe(CO)_{10}$ (0.38 mmol; 201 mg) and ^tBuNC (0.42 mmol; 46 μL) were taken up in benzene (20 mL) at room temperature. PdO catalyst (5 mg) was added to the reaction vessel, and the reaction progress was monitored by IR spectroscopy. The reaction was considered complete after 10 min, and the solution, after passage through a cellulose column to remove PdO, was pumped to dryness under vacuum. Final purification was achieved by recrystallization from acetone/hexane (−20 °C) to yield a yellow crystalline material. The purity of the complex was confirmed by a combination of IR and NMR spectroscopy and comparison with the spectral properties of $Re_2(CO)_9(CNBu^t)$ and $Mn_2(CO)_9(CNBu^t)$.[1] IR (hexane) (2200–1600-cm^{-1} region): 2182 (w), 2090 (m), 2041 (s), 2024 (w), 2002 (vs), 1977 (m), 1963 (s), 1957 (s) cm^{-1}. UV (holium standard 361 nm): 322 nm. ^1H NMR (C_6D_6): 0.75 s (^tBuNC) ppm.

Synthesis of $(CO)_5MnRe(CO)_4P(CH_2C_6H_5)_3{}^{12}$ (2). $MnRe(CO)_{10}$ (0.19 mmol; 100 mg) and $P(CH_2C_6H_5)_3$ were taken up in CH_2Cl_2 (25 mL). Me_3NO (0.21 mmol; 15 mg) was added to the solution at room temperature. Reaction progress was monitored by IR spectroscopy and considered complete when the IR spectrum no longer changed with time. Purification of the required product was achieved by column chromatography (silica; C_6H_6/hexane as eluent) and crystallization from acetone/hexane (−20 °C) to yield a yellow crystalline material. IR and NMR spectroscopy and analysis confirmed the purity of the complex. Anal. Calcd for $C_{30}H_{21}MnO_9PRe$: C, 45.18; H, 2.65. Found: C, 45.15; H, 2.59. IR (hexane) (2200–1600-cm^{-1} region): 2092 (w), 2029 (m), 2009 (sh), 2003 (m), 1991 (s), 1995 (m), 1967 (w), 1948 (w) cm^{-1}. ^1H NMR (C_6D_6): 3.15 d $(CH_2C_6H_5)_3$, 7.05 m $(CH_2C_6H_5)_3$ ppm. ^{31}P NMR (C_6D_6): 4.5 ppm.

Synthesis of $(CO)_5MnRe(CO)_3(CNBu^t)(PPh_3)$ (3). $MnRe(CO)_9(CNBu^t)$ (0.27 mmol; 150 mg) and PPh_3 (0.30 mmol; 78 mg) were dissolved in C_6H_6 (20 mL), and the solution was heated to 45 °C. Me_3NO (0.43 mmol; 32 mg) was added to the stirred solution, and the reaction was allowed to proceed in the dark. When the IR spectrum no longer changed with time, the reaction was considered to be complete. Solvent was removed from the cooled solution under vacuum. The purified product was isolated by column chromatography (silica; C_6H_6/hexane as eluent), and red-brown crystals were obtained from an acetone/hexane (−20 °C) mixture. The purity of the complex was confirmed by analysis and IR and NMR spectroscopy. Anal. Calcd for $C_{31}H_{24}MnNO_8PRe$: C, 45.93; H, 2.98; N, 1.73. Found: C, 44.98; H, 2.63; N, 1.86. IR (CH_2Cl_2) (2200–1600-cm^{-1} region): 2163 (w), 2065 (m), 2059 (sh), 2007 (m), 1968 (vs), 1948 (sh) cm^{-1}. ^1H NMR (C_6D_6): 0.75 s (^tBuNC), 6.92 and 7.03 m (Ph) ppm. ^{31}P NMR (C_6D_6): 12.83 ppm.

Crystallographic Analyses. Crystals were grown from acetone/hexane solutions and suitable specimens mounted on glass fibers. Cell determinations, using 25 high-order reflection, and data collections were done on Enraf-Nonius CAD4 four-circle diffractometers equipped with graphite monochromators. Mo Kα radiation was used for compounds **2** and **3** and Cu Kα for **1** since tthis compound exhibited excessive decay with Mo Kα.

Data reduction included corrections for Lorentz polarization and background. Crystal decay was corrected linearly for compounds **1** and **2**, while a fifth order polynomial was used for compound **3**. Empirical absorption corrections[13] were applied to the intensity data of compounds **1** and **2**. Analytical absorption corrections, calculated by the ABSORP routine of the NRCVAX[14] set of programs, were applied for compound **3**. This routine requires that the faces of the crystal be indexed and measured. It then uses this information to calculate the necessary corrections by a Gaussian integration method.

Unit cell parameters and details of the data collections are given in Table I. The structures were solved using Patterson and difference Fourier techniques. For **1** and **2** blocked diagonal matrices were used, and for **3** a full matrix was used in the least-squares refinement. Hydrogen atom positions were generated geometrically (C–H = 1.08 Å, H–C–H = 109.5°) and fixed relative to the atom to which it was bonded in the final cycles of refinement. The SHELX[15,16] suit of programs were used for structure solution and refinement, and SHAKAL 88[17] was used to produce the molecular diagrams.

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Table III. Fractional Atomic Coordinates (×10⁴; ×10⁵ for Re) and Equivalent Isotropic Temperature Factors (Å² × 10³) for **2**

	x/a	y/b	z/c	U_{eq}[a]		x/a	y/b	z/c	U_{eq}[a]
Rea	22648 (4)	16063 (4)	12150 (4)	44 (0)	ReB	31309 (4)	21494 (4)	62346 (4)	52 (0)
MnA	1441 (2)	−356 (1)	1279 (1)	42 (1)	MnB	4127 (2)	1852 (2)	7575 (1)	49 (1)
P1A	2734 (3)	3217 (2)	1167 (2)	42 (1)	P1B	2102 (3)	2459 (3)	5274 (2)	50 (1)
O1A	664 (8)	−2269 (7)	1263 (6)	76 (3)*	O1B	5178 (9)	1662 (9)	8862 (6)	87 (4)
O2A	15 (8)	909 (7)	275 (6)	84 (3)*	O2B	3031 (10)	3709 (8)	7593 (7)	97 (4)
O3A	3305 (9)	−43 (8)	−68 (6)	83 (4)	O3B	5926 (10)	3183 (9)	6396 (7)	114 (4)*
O4A	2833 (8)	−1314 (7)	2406 (6)	79 (3)	O4B	5130 (10)	89 (9)	7284 (7)	100 (4)
O5A	−182 (9)	−361 (8)	2659 (7)	86 (4)	O5B	2141 (9)	539 (8)	8547 (7)	104 (4)*
O6A	4652 (7)	799 (7)	949 (6)	74 (3)	O6B	5429 (9)	1698 (12)	5396 (7)	133 (5)
O7A	2307 (8)	601 (7)	2925 (6)	72 (3)	O7B	2669 (9)	−157 (8)	6852 (7)	88 (4)
O8A	−254 (8)	1984 (8)	1640 (7)	89 (3)	O8B	1029 (8)	2289 (8)	7394 (6)	88 (3)
O9A	2468 (9)	2365 (7)	−535 (6)	77 (3)	O9B	3895 (8)	4409 (8)	5634 (7)	89 (3)
C1A	963 (11)	−1504 (10)	1276 (8)	57 (4)*	C1B	4730 (13)	1699 (11)	8358 (10)	70 (5)
C2A	597 (11)	411 (10)	668 (8)	62 (4)*	C2B	3437 (13)	2998 (12)	7586 (10)	74 (5)
C3A	2598 (13)	−157 (10)	449 (10)	64 (5)	C3B	5221 (15)	2643 (13)	6854 (10)	96 (6)*
C4A	2315 (11)	−924 (10)	1942 (8)	53 (4)	C4B	4735 (13)	760 (11)	7395 (9)	67 (5)
C5A	418 (12)	−345 (10)	2128 (10)	61 (5)	C5B	2925 (13)	1063 (12)	8147 (10)	83 (5)*
C6A	3840 (12)	1141 (9)	1021 (8)	57 (4)	C6B	4632 (13)	1893 (14)	5646 (9)	84 (5)
C7A	2267 (11)	984 (9)	2276 (9)	47 (4)	C7B	2811 (11)	695 (11)	6625 (9)	62 (5)
C8A	627 (13)	1837 (10)	1477 (9)	65 (4)	C8B	1769 (12)	2235 (10)	6981 (9)	59 (4)
C9A	2336 (11)	2106 (9)	136 (9)	51 (4)	C9B	3583 (10)	3579 (11)	5867 (9)	58 (4)
C10A	2641 (10)	3249 (8)	2126 (7)	43 (3)*	C10B	900 (10)	3256 (9)	5323 (8)	56 (4)*
C12A	1817 (6)	4760 (7)	2326 (5)	79 (2)*	C12B	1555 (8)	5054 (9)	4677 (5)	90 (2)*
C13A	1914 (6)	5698 (7)	2383 (5)	79 (2)*	C13B	1827 (8)	5988 (9)	4692 (5)	90 (2)*
C14A	2958 (6)	6116 (7)	2327 (5)	79 (2)*	C14B	1644 (8)	6128 (9)	5388 (5)	90 (2)*
C15A	3905 (6)	5596 (7)	2213 (5)	79 (2)*	C15B	1190 (8)	5334 (9)	6068 (5)	90 (2)*
C16A	3808 (6)	4659 (7)	2155 (5)	79 (2)*	C16B	918 (8)	4400 (9)	6053 (5)	90 (2)*
C11A	2763 (6)	4241 (7)	2212 (5)	79 (2)*	C11B	1101 (8)	4260 (9)	5358 (5)	90 (2)*
C17A	1802 (10)	4238 (9)	782 (7)	48 (4)*	C17B	1436 (10)	1279 (9)	5315 (8)	56 (4)*
C19A	709 (7)	3968 (6)	−113 (5)	76 (2)*	C19B	612 (6)	1532 (7)	4160 (6)	83 (2)*
C20A	551 (7)	4177 (6)	−854 (5)	76 (2)*	C20B	−299 (6)	1548 (7)	3826 (6)	83 (2)*
C21A	1286 (7)	4857 (6)	−1480 (5)	76 (2)*	C21B	−1373 (6)	1383 (7)	4271 (6)	83 (2)*
C22A	2179 (7)	5329 (6)	−1366 (5)	76 (2)*	C22B	−1538 (6)	1201 (7)	5052 (6)	83 (2)*
C23A	2338 (7)	5120 (6)	−626 (5)	76 (2)*	C23B	−629 (6)	1186 (7)	5386 (6)	83 (2)*
C18A	1602 (7)	4440 (6)	1 (5)	76 (2)*	C18B	446 (6)	1351 (7)	4940 (6)	83 (2)*
C24A	4071 (9)	3870 (8)	593 (7)	48 (4)*	C24B	2770 (10)	3107 (9)	4278 (7)	58 (4)*
C26A	5702 (7)	3201 (6)	−43 (4)	67 (2)*	C26B	4842 (9)	3505 (6)	3871 (5)	127 (2)*
C27A	6668 (7)	2678 (6)	−50 (4)	67 (2)*	C27B	5903 (9)	3286 (6)	3575 (5)	127 (2)*
C28A	7048 (7)	2211 (6)	626 (4)	67 (2)*	C28B	6052 (9)	2421 (6)	3402 (5)	127 (2)*
C29A	6462 (7)	2268 (6)	1310 (4)	67 (2)*	C29B	5139 (9)	1775 (6)	3524 (5)	127 (2)*
C30A	5496 (7)	2792 (6)	1317 (4)	67 (2)*	C30B	4077 (9)	1994 (6)	3818 (5)	127 (2)*
C25A	5116 (7)	3258 (6)	641 (4)	67 (2)*	C25B	3928 (9)	2859 (6)	3992 (5)	127 (2)*

[a] See footnote *a* of Table II.

Table IV. Fractional Atomic Coordinates (×10⁴; ×10⁵ for Re and Mn) and Equivalent Isotropic Temperature Factors (Å² × 10³) for **3**

	x/a	y/b	z/c	U_{eq}[a]		x/a	y/b	z/c	U_{eq}[a]
Rb	73806 (1)	37795 (3)	19332 (1)	45 (0)	C11	5946 (6)	1099 (10)	3390 (6)	140 (4)
Mn	62612 (5)	24740 (11)	5915 (5)	56 (0)	C12	7197 (5)	−113 (12)	3698 (6)	163 (4)
P	8209 (1)	4733 (2)	3052 (1)	48 (0)	C13	6110 (7)	−743 (10)	2631 (5)	180 (5)
N	6769 (3)	1447 (6)	2736 (3)	57 (1)	C14	8739 (3)	6365 (6)	3046 (3)	51 (1)
O1	5042 (3)	1250 (6)	−715 (3)	105 (2)	C15	9538 (3)	6658 (7)	3501 (4)	65 (2)
O2	5935 (3)	5404 (6)	87 (3)	95 (2)	C16	9872 (4)	7926 (8)	3484 (4)	79 (2)
O3	5096 (2)	2683 (5)	1307 (3)	84 (1)	C17	9437 (5)	8902 (8)	3012 (5)	98 (3)
O4	6843 (3)	−266 (5)	1271 (3)	86 (2)	C18	8651 (5)	8642 (7)	2550 (5)	103 (3)
O5	7702 (3)	2481 (6)	207 (3)	95 (2)	C19	8309 (4)	7370 (7)	2573 (4)	81 (2)
O6	5998 (3)	5940 (5)	1703 (3)	95 (2)	C20	7717 (3)	5233 (6)	3653 (3)	52 (2)
O7	8007 (3)	5669 (6)	1045 (3)	100 (2)	C21	8148 (4)	5915 (7)	4275 (4)	73 (2)
O8	8687 (2)	1673 (5)	1909 (3)	78 (1)	C22	7771 (4)	6361 (8)	4723 (4)	86 (2)
C1	5526 (3)	1731 (8)	−209 (4)	72 (2)	C23	6952 (4)	6117 (8)	4534 (4)	81 (2)
C2	6063 (4)	4283 (9)	290 (4)	72 (2)	C24	6519 (4)	5426 (7)	3918 (4)	69 (2)
C3	5548 (3)	2604 (7)	1032 (3)	65 (2)	C25	6898 (3)	4974 (7)	3485 (3)	63 (2)
C4	6623 (4)	792 (8)	1029 (4)	64 (2)	C26	9030 (3)	3560 (6)	3597 (3)	52 (1)
C5	7145 (3)	2504 (7)	357 (3)	64 (2)	C27	9677 (3)	3337 (7)	3388 (4)	64 (2)
C6	6514 (4)	5109 (8)	1807 (3)	64 (2)	C28	10288 (4)	2410 (8)	3769 (5)	88 (2)
C7	7767 (3)	4953 (8)	1407 (4)	68 (2)	C29	10266 (5)	1728 (9)	4334 (5)	95 (2)
C8	8201 (3)	2441 (7)	1925 (3)	58 (2)	C30	9640 (5)	1917 (8)	4534 (4)	92 (2)
C9	6972 (3)	2308 (6)	2444 (3)	50 (1)	C31	9020 (4)	2847 (7)	4174 (4)	76 (2)
C10	6487 (4)	406 (8)	3103 (4)	68 (2)					

[a] See footnote *a* of Table II.

Final positional parameters are to be found in Tables II–IV.

The crystal structures for **1** and **2** show severe systematic errors. Structure **1**, in particular, showed both absorption and crystal decay in

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(17) Keller, E. SHAKAL 88. Kristal. Inst. der Univ. Freiburg, Germany, 1988.

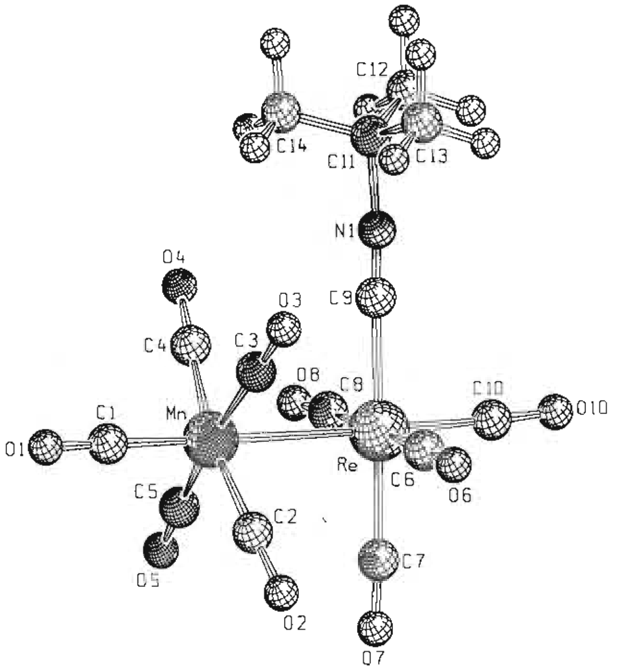

Figure 1. Ortep diagram of $(CO)_5MnRe(CO)_4(CNBu^t)$.

the X-ray beam, while **2** was primarily affected by absorption effects. Although this affects the overall quality of the structures the metal–metal bond distances remain reasonably reliable. The asymmetric units for both crystals also contain two molecules that show only conformational differences. The routine MISSYM of the NRCVAX[14] set of programs did not produce any evidence of higher symmetry or erroneous space group assignment.

Results and Discussion

The synthetic strategies employed in the synthesis of the substituted Mn–Re have been discussed elsewhere.[1,12,18] In all three complexes purity was confirmed by a combination of analytical data (C, H, N) and IR and NMR (^{1}H, ^{31}P) spectroscopy. The spectroscopic data readily permit an evaluation of the presence of the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$-substituted complexes. No presence of these impurities was detected in the crystalline materials **1**–**3** used in this study.

The crystal structure determination of the three complexes **1**–**3** reveals that in every instance substitution has taken place at the Re atom as shown in Figures 1–3. The figures also indicate the numbering system used in the discussion. Pertinent bond length and bond angle data are shown in Tables V and VI.

From the data the following conclusions can be drawn: (1) The Mn–Re bond lengths are all close to 2.96 Å. This value is little affected by the axial, equatorial, or the axial–equatorial substitution patterns. A comparison with data on other related substituted dimer carbonyl complexes (Table VII) reveals that the M–M bond lengthens only slightly on replacement of CO by other similar ligands in the dimer. Marked lengthening is noted for $Re(CO)_5Mn(CO)_3(^iPrDAB)$[11] (see below). (2) There are no bridging carbonyl groups. The ligands on the metal atoms are in a staggered arrangement with C–Mn–Re–C torsion angles in the range 45 ± 5° for all three structures. (One exception: C4–Mn–Re–C6/C7 = 45° ± 9° for **2**). The equatorial CO ligands on Mn bend in 4–5° toward Re. The ligands on Re bend in less toward Mn. In **1** the bending is 1–2°, while for **2** and **3** (with an axial PR_3 group) the bending increases to 3°. It is not clear whether this arises from electronic effects[19] or from a steric effect. (3) Typical M–CO bond lengths are observed; i.e., M–C(O) bonds that are cis to the Mn–Re bond and are trans to a CO group are longer than M–C(O) bond lengths that are trans to a M–M bond or trans to the ^{t}BuNC group. (4) The position of the ligands in the coordination sphere is that expected from the steric/electronic properties of ^{t}BuNC and the phosphine ligand ($P(CH_2C_6H_5)_3$, PPh_3). Thus, the small ^{t}BuNC[20] can be accommodated in the electronically favored equatorial site, while the bulkier phosphines (PPh_3, $\theta = 145°$; $P(CH_2C_6H_5)_3$, $\theta = 165°$ [21]), which are less nucleophilic than the isonitriles, preferentially occupy the less sterically demanding axial site. (5) Although 16 possible isomers corresponding to the formula $MnRe(CO)_8(PPh_3)(CNBu^t)$ are possible, only three isomers are anticipated (Figure 4) once the nature of the starting materials and ligands is defined. The structural analysis confirms that the isomer synthesized, **4b**, is that expected on both electronic and steric grounds and from a knowledge of the reactivity of $MnRe(CO)_{10}$.

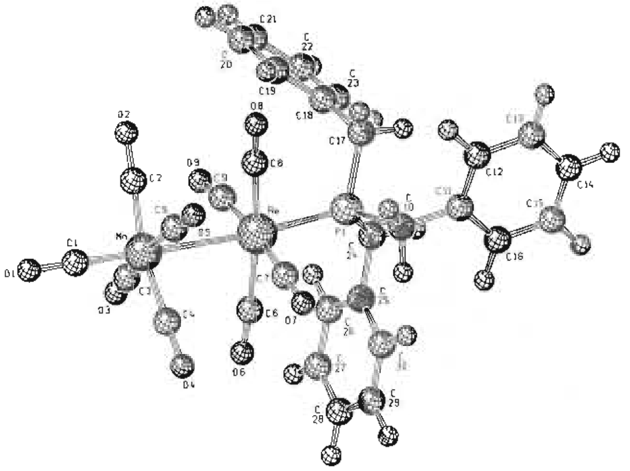

Figure 2. Ortep plot of $(CO)_5MnRe(CO)_4P(CH_2C_6H_5)_3$.

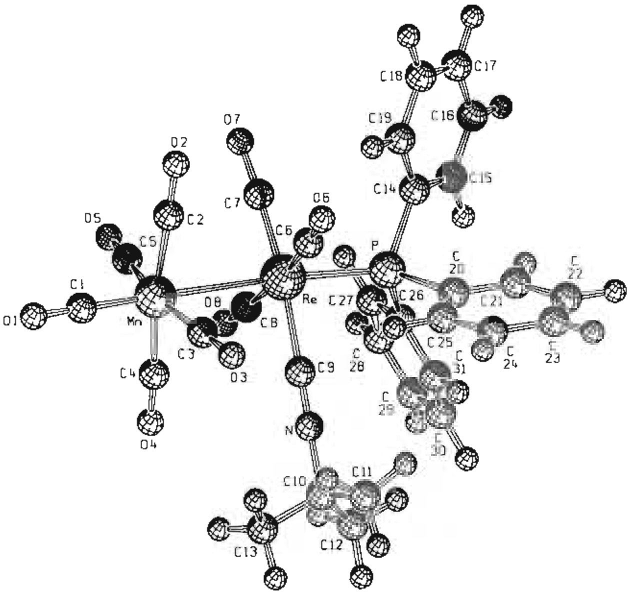

Figure 3. Ortep plot of $(CO)_5MnRe(CNBu^t)(PPh_3)$.

The crystallographic data indicate that the M–M bond length gives little information about the position or degree of substitution on the dimer. From earlier studies we have shown that as steric

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Table V. Selected Bond Lengths (Å) for **1–3**

	1		**2**		
	A	B	A	B	**3**
Mn–Re	2.960 (3)	2.966 (3)	2.954 (2)	2.958 (2)	2.969 (1)
Mn–C1	1.800 (24)	1.776 (18)	1.756 (16)	1.750 (20)	1.798 (7)
Mn–C2	1.788 (23)	1.808 (20)	1.778 (14)	1.838 (18)	1.834 (8)
Mn–C3	1.844 (24)	1.834 (20)	1.849 (16)	1.779 (15)	1.830 (7)
Mn–C4	1.829 (21)	1.808 (22)	1.788 (15)	1.777 (14)	1.839 (8)
Mn–C5	1.844 (20)	1.852 (21)	1.855 (16)	1.837 (18)	1.820 (6)
Mn–C_{av}[a]	1.83 (2)	1.83 (2)	1.82 (2)	1.81 (2)	1.831 (7)
Re–C6	2.021 (23)	1.983 (22)	2.065 (16)	2.065 (16)	1.943 (7)
Re–C7	1.942 (20)	1.912 (20)	1.901 (16)	1.951 (15)	1.870 (8)
Re–C8	1.868 (18)	1.959 (23)	2.009 (14)	2.009 (14)	1.955 (6)
Re–C9			1.909 (16)	1.952 (15)	
Re–C_{cis}[b]	1.98 (2)	1.97 (2)	1.97 (2)	1.99 (2)	1.949 (7)
Re–C10	1.934 (18)	1.849 (16)			
Re–P			2.351 (4)	2.349 (4)	2.371 (2)
C9–N	1.085 (24)	1.115 (29)			1.161 (6)
Re–CNBu^t	2.117 (24)	2.128 (19)			2.057 (6)

[a] Average of cis CO groups. [b] Average of CO groups cis to ^{t}BuNC *or* $P(CH_2C_6H_5)_3$.

Table VI. Selected Bond Angles (deg) for **1–3**

	1		**2**		
	A	B	A	B	**3**
Re–Mn–C(1)	178.9 (8)	174.7 (6)	177.7 (5)	178.9 (5)	176.1 (2)
Re–Mn–C(2)	84.2 (7)	86.9 (6)	82.7 (5)	84.4 (6)	83.2 (2)
Re–Mn–C(3)	83.1 (7)	82.4 (6)	84.8 (5)	82.0 (7)	81.9 (2)
Re–Mn–C(4)	84.9 (9)	83.3 (6)	86.9 (5)	85.0 (6)	86.6 (2)
Re–Mn–C(5)	87.3 (7)	85.5 (6)	84.2 (5)	87.2 (6)	84.3 (2)
Mn–Re–C(6)	91.4 (6)	89.0 (6)	87.6 (4)	90.0 (5)	86.8 (2)
Mn–Re–C(7)	87.4 (7)	89.0 (6)	88.0 (4)	88.2 (5)	89.3 (2)
Mn–Re–C(8)	89.0 (6)	87.7 (6)	84.1 (4)	80.6 (5)	86.9 (2)
Mn–Re–C(9)	177.8 (5)	178.3 (5)	87.6 (4)	88.0 (5)	86.4 (2)
Mn–Re–C(10)	87.2 (5)	87.3 (5)			
Mn–Re–P			174.2 (1)	171.3 (1)	175.2 (0)
C(1)–Mn–C(2)	96.8 (10)	97.0 (9)	95.8 (7)	95.0 (8)	95.5 (3)
C(1)–Mn–C(3)	95.9 (10)	93.8 (9)	93.4 (7)	97.0 (8)	94.5 (3)
C(1)–Mn–C(4)	94.8 (10)	93.1 (8)	94.6 (7)	95.5 (8)	94.9 (3)
C(1)–Mn–C(5)	93.0 (9)	98.2 (8)	97.6 (6)	93.8 (8)	99.4 (3)
C(2)–Mn–C(3)	88.0 (10)	88.5 (9)	90.8 (7)	87.9 (7)	91.2 (3)
C(2)–Mn–C(4)	167.3 (10)	169.1 (9)	169.0 (8)	169.4 (8)	169.4 (3)
C(2)–Mn–C(5)	91.2 (9)	89.0 (9)	90.0 (7)	92.4 (7)	88.2 (3)
C(3)–Mn–C(4)	91.0 (10)	91.5 (9)	92.0 (7)	89.2 (8)	89.9 (3)
C(3)–Mn–C(5)	172.2 (10)	168.6 (8)	168.8 (8)	169.2 (10)	166.2 (3)
C(4)–Mn–C(5)	88.1 (9)	88.8 (9)	85.2 (7)	88.6 (7)	88.2 (3)
C(6)–Re–C(7)	91.7 (8)	90.0 (10)	86.6 (6)	86.4 (6)	88.9 (3)
C(6)–Re–C(8)	178.0 (8)	175.4 (9)	171.1 (5)	169.4 (6)	172.5 (3)
C(6)–Re–C(9)	90.7 (8)	89.9 (8)	88.8 (6)	90.0 (6)	95.6 (2)
C(6)–Re–C(10)	88.5 (8)	92.9 (10)			
C(7)–Re–C(8)	92.1 (8)	92.2 (7)	89.8 (6)	88.4 (6)	86.9 (3)
C(7)–Re–C(9)	176.4 (9)	175.5 (8)	173.8 (6)	174.8 (6)	173.6 (3)
C(7)–Re–C(10)	89.7 (8)	87.2 (9)			
C(8)–Re–C(9)	91.4 (8)	89.7 (9)	94.1 (6)	94.5 (6)	88.2 (2)
C(8)–Re–C(10)	90.0 (8)	89.7 (9)			
C(9)–Re–C(10)	90.7 (7)	94.0 (7)			

crowding increases, bond lengthening can take place, but in complexes **1–3** the steric crowding of the ligands must be minimal. This of course provides strong evidence for a bond length of ±2.96 Å for $MnRe(CO)_{10}$ as originally observed.[5] The bond length obtained from the crystal structure of $Re(CO)_5Mn(CO)_3$-(^{i}PrDAB) (d_{Mn-Re} = 3.012 Å[11]) is unusual. The ligand which occupies the diequatorial positions on Mn results in excessive steric crowding and subsequent Mn–Re bond lengthening.

It is to be noted that difficulties were experienced by Rheingold and co-workers in analyzing the data for $MnRe(CO)_{10}$.[8] The disorder problem associated with Mn–Re interchange (point group *I*2/*a*) was dealt with by four different strategies, but all strategies did give a bond length of ±2.91 Å. Our data would suggest that, notwithstanding the strategies employed, the bond length data must be treated with caution.

Since IR spectroscopy is one of the most convenient methods of establishing substitution patterns of $M_2(CO)_{10-x}L_x$ (M = Mn, Re; L = ligand), we have over the years attempted to correlate the IR spectra with dimer isomer composition.[22] Although the IR spectroscopic data can be used to establish the position of L (axial versus equatorial) in the monosubstituted dimer, the technique does not unequivocally establish whether substitution has occurred at Mn or Re. Further, six possible disubstituted dimers of $M_2(CO)_8L_2$ are possible (see Figure 5), and although there is a correlation between the IR patterns and crystallographic data for isomers a, c, and f, the data base presently does not extend to the other isomers.[23]

Our crystallographic data on **3** now permit a correlation between the geometry associated with isomer d and IR spectroscopic data. The spectrum of **3** is shown in Figure 6. It is to be noted that complexes with geometry as shown for isomer e have been

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(23) Gard, D. R.; Brown, T. L. *Organometallics* **1982**, *1*, 1143.

Table VII. Effect of Substitution on Metal–Metal Bond Lengths

complex	M–M, Å
$Re_2(CO)_{10}$	3.041 (11)[a]
$Re_2(CO)_9(CNBu^t)$	3.048 (1)[b]
$Re_2(CO)_9C(OMe)(SiPh_3)$	3.052 (1)[c]
$Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2$	3.047 (0)[b]
$Re_2(CO)_8(PMe_2Ph)_2$	3.044 (1)[d]
$CpMo(CO)_3Re(CO)_5$	3.172 (1)[e]
$CpMo(CO)_3Re(CO)_4(CNBu^t)$	3.188 (1)[e]
$CpFe(CO)_2Re(CO)_5$	2.888 (1)[f]
$CpFe(CO)_2Re(CO)_4(CNBu^t)$	2.893 (1)[g]
$MnRe(CO)_{10}$	2.909 (1),[h] 2.96[i]
$Mn(CO)_5Re(CO)_4(CNBu^t)$	2.963 (3)[j]
$Mn(CO)_5Re(CO)_4P(CH_2C_6H_5)_3$	2.954 (2)[j]
$Mn(CO)_5Re(CO)_4[C(OMe)CH_3]$	2.972 (1)[k]
$Mn(CO)_5Re(CO)_3(PPh_3)(CNBu^t)$	2.969 (1)[j]
$Mn(CO)_3(^iPrDAB)Re(CO)_5$	3.012 (2)[l]
$Mn_2(CO)_{10}$	2.904 (1),[m] 2.895 (1)[m]
$Mn_2(CO)_9P(C_6H_5)_2H$	2.910 (2)[n]
$CpFe(CO)_2Mn(CO)_5$	2.841 (4),[o] 2.845 (4)[o]
$CpFe(CO)_2Mn(CO)_4(CNBu^t)$	2.841 (1)[g]
$CpMo(CO)_3Mn(CO)_5$	3.083 (8)[p]
$CpMo(CO)_3Mn(CO)_4P(OMe)_3$	3.112 (1)[p]

[a] See ref 2. [b] Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1985**, *4*, 914. [c] Schmidt, U.; Ackerman, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 232. [d] Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277. [e] See ref 10. [f] Johnston, P.; Dickson, C.-A.; Markwell, A. J.; Denner, L.; Boeyens, J. C. A.; Coville, N. J. *Inorg. Chim. Acta* **1988**, *144*, 185. [g] Johnston, P.; Hutchings, G. J.; Denner, L.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1987**, *6*, 1292. [h] See ref 8. [i] See ref 5. [j] This work. [k] See ref 7. [l] See ref 11. [m] See refs 3 and 4. [n] Giordano, R.; Sappa, E.; Tiripicchio, A.; Camellini, M. T.; Mays, M. J.; Brown, M. P. *Polyhedron* **1989**, *8*, 1855. [o] Hensen, P. J.; Jacobson, R. A. *J. Organomet. Chem.* **1966**, *6*, 389. [p] Ingham, W. L.; Billing, D. G.; Levendis, D. C.; Coville, N. J. *Inorg. Chim. Acta* **1991**, *187*, 17.

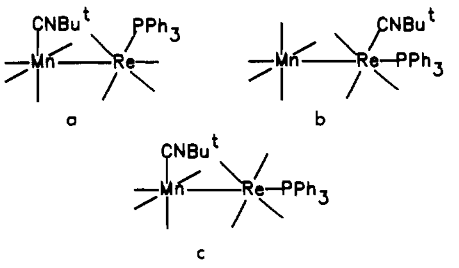

Figure 4. Possible isomers for $MnRe(CO)_8(CNBu^t)$.

synthesized (e.g. $Re_2(CO)_8L_2$, L = $P(^nBu_3)$, PPh_3[24]) but so far no isomer corresponding to isomer b has to our knowledge been reported.

Conclusion

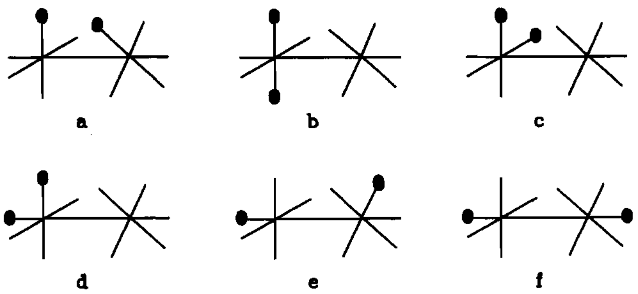

Figure 5. Possible disubstituted dimers of $M_2(CO)_8L_2$ (● = position of substitution of CO by L).

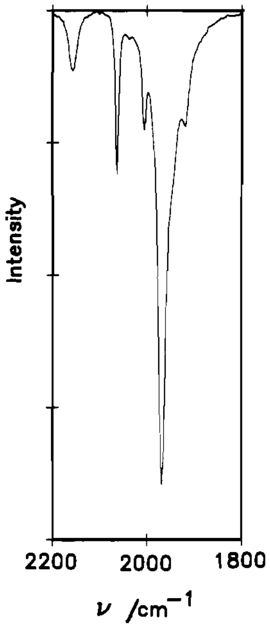

Figure 6. IR spectrum of $MnRe(CO)_8(CNBu^t)(PPh_3)$.

A comprehensive investigation of the physical and chemical properties of $MnRe(CO)_{10}$ and its substituted derivatives[25] has revealed that certain properties associated with $MnRe(CO)_{10}$ are not necessarily additive properties determined from a knowledge of the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ parent complexes. These differences appear to relate to the polarity induced in the heteronuclear dimer which is not observed in the homonuclear dimers. However, the many studies (Table VII), including this one, suggest that crystallographic data are little influenced by these polarity changes and that the metal–metal bond length of heteronuclear dimers can be predicted from the bond lengths of the related homonuclear dimers.

Acknowledgment. We wish to thank the University and the FRD for financial support.

Supplementary Material Available: Detailed listings of crystallographic parameters (Table S1), anisotropic thermal factors (Tables S2–S4), and comprehensive bond distances (Tables S5–S7) and angles (Tables S8–S10) (12 pages). Ordering information is given on any current masthead page.

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