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Rhenium complexes from alkynes. X-Ray crystal structures of $Re_2(\mu\text{-}2\eta^1,\eta^4\text{-}C_4Ph_4)(CO)_7$ and $Re\{C,O\text{-}CH{=}C[Re(CO)_4(NMe_3)]C(OMe)O\}(CO)_4$

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Abstract

The molecular structure of $Re_2(\mu\text{-}2\eta^1,\eta^4\text{-}C_4Ph_4)(CO)_7$ obtained from $Re_2(CO)_8(NCMe)_2$ and C_2Ph_2, consists of an $Re_2(CO)_7$ unit [Re–Re 2.874(1) Å] bridged by a $2\eta^1,\eta^4\text{-}C_4Ph_4$ ligand, as proposed by earlier workers. Methyl propiolate is inserted into the Re–Re bond of $Re_2(CO)_9(NCMe)$, as shown by the molecular structure of the NMe_3 derivative of the product; the NMe_3 ligand is attached to the non-chelated Re atom [Re–N 2.31(1) Å].

Key words: Rhenium; Alkyne; Crystal structure; Amine; Carbonyl; Vinyl

1. Introduction

Although the reactions between metal carbonyls and alkynes have been the source of many interesting and novel complexes, these have been relatively little studied in the case of rhenium. Early reports of the reaction between $Re_2(CO)_{10}$ and diphenylethyne [1,2] describe the formation of three complexes, two of which were identified with the aid of X-ray structure determinations [1,2]. Adams [3] has described some chemistry of rhenium carbonyls with aminoethynes and more recently, has reported an unusual insertion of HC_2CO_2Me into the Re–Re bond of the binuclear carbonyl [4]. In connection with other work to be reported elsewhere, we have had occasion to repeat these reactions, obtaining two related complexes, the molecular structures of which form the subject of this paper.

2. Results and discussion

We carried out a reaction between the "activated" rhenium carbonyl, $Re_2(CO)_8(NCMe_2)$, and C_2Ph_2 in refluxing dichloromethane for 24 h. From the reaction mixture we were able to isolate the three complexes $Re_2(\mu\text{-}C_4Ph_4)(CO)_7$ (**1**) (8%), $Re_2(CO)_5(C_4Ph_4)(C_2Ph_2)$ (**2**) (7%) and $Re_2(CO)_4(C_6Ph_6)(C_2Ph_2)$ (**3**) (18%). While the latter two have been structurally characterized, we took the advantage of having a crystalline sample of **1** to determine its molecular structure, thereby confirming the suggestions made earlier [1] concerning the nature of this complex.

2.1. Molecular structure of $Re_2(\mu\text{-}C_4Ph_4)(CO)_7$ (1)

A molecule of **1** is depicted in Fig. 1 and selected bond parameters are collected in Table 1, together with corresponding data for **2**. It can be seen that two C_2Ph_2 molecules have joined with one Re to form a rhenacyclopentadiene [Re(2)–C(1,4) 2.207(7), 2.203(8) Å] which is attached to the second Re atom in the η^4 mode [Re(1)–C(1–4) 2.25(1)–2.342(7) Å]. An Re–Re

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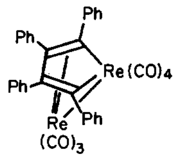
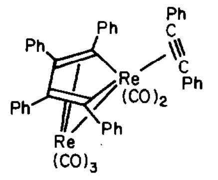


(1)



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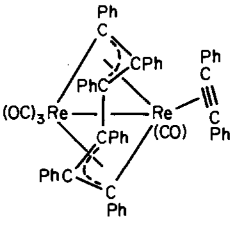

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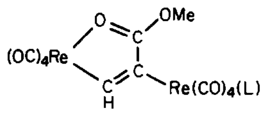

(4) L = CO

(5) L = NMe3

bond [2.874(1) Å] joins the two atoms. Three CO groups are attached to Re(1), four to Re(2); CO(13) is somewhat closer to its Re atom [1.888(9) Å] than the other five [average Re–C 1.95_3 Å], probably because of the competing electronic requirements of the Re–Re bond, to which it is *trans*. The geometry about each Re atom is approximately octahedral if the Re–Re bond occupies a coordination site on Re(1) but not on Re(2). Around Re(2), the angle subtended by by C(1, 4) is 75.0(3)° and by CO(21, 22) and CO(23, 24) are 94.3(4) and 173.3(4)°, respectively. The latter appear to be pushed away from the ReC$_4$ ring by the bulky Ph groups. The angles at Re(1) subtended by the CO groups range between 85.5 and 89.5(4)°, and from CO(11, 12) to the midpoints of the C(3, 4) and C(1, 2), bonds are 103.7(3) and 108.6(4)°, respectively. The Re(2)–Re(1)–CO(13) angle is 163.4(3)°.

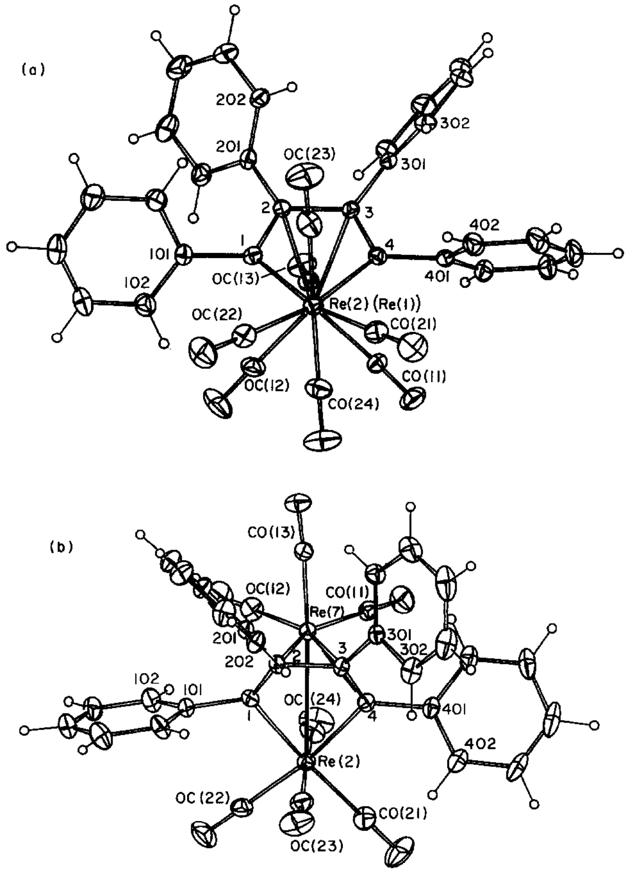

Fig. 1. Plot of a molecule of Re$_2$(μ-2η^1,η^4-C$_4$Ph$_4$)(CO)$_7$ (1) (a) down and (b) normal to the Re–Re bond; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

TABLE 1. Some bond parameters for complexes **1** and **2** [2]

	1	**2**
Bond lengths (Å)		
Re(1)-Re(2)	2.874(1)	2.878(1)
Re(1)-C(1)	2.25(1)	2.255(5)
Re(1)-C(2)	2.322(8)	2.307(5)
Re(1)-C(3)	2.342(7)	2.351(5)
Re(1)-C(4)	2.320(7)	2.359(5)
Re(1)-C(24)	2.85(1)	
Re(2)-C(1)	2.207(7)	2.099(5)
Re(2)-C(4)	2.203(8)	2.170(5)
C(1)-C(2)	1.40(1)	1.407(7)
C(2)-C(3)	1.48(1)	1.446(7)
C(3)-C(4)	1.38(1)	1.388(7)
Bond angles (°)		
Re(2)-Re(1)-C(13)	163.4(3)	163.6(2)
C(21)-Re(2)-C(1)	167.5(3)	124.0(3)
C(22)-Re(2)-C(4)	167.6(3)	146.7(3)
C(1)-Re(2)-C(4)	75.0(3)	75.4(2)
C(23)-Re(2)-C(24)	173.3(4)	
C(21)-Re(2)-C(22)	94.3(3)	84.8(3)
C(11)-Re(1)-C(12)	87.3(4)	88.4(3)
C(11)-Re(1)-C(13)	89.5(4)	88.8(3)
C(12)-Re(1)-C(13)	85.5(4)	86.9(4)
Re(2)-C(24)-O(24)	170(1)	

The five-membered ReC$_4$ ring does not exhibit any unusual features. As found for **2**, there is an alternation in C–C distances [C(1)–C(2) 1.40(1), C(2)–C(3) 1.48(1), C(3)–C(4) 1.38(1) Å]. In **1**, two CO groups occupy the coordination position occupied by the C$_2$Ph$_2$ molecule in **2**. Atoms C(21, 22) are respectively *trans* to C(1, 4), with angles at Re(2) being 167.5(3) and 167.6(3)°. Each metal atom has an 18-electron configuration.

In summary, this structure determination has confirmed the previously suggested structure for **1**: there are few changes resulting from the replacement of two CO groups in **1** by the C$_2$Ph$_2$ ligand found in **2**.

The reaction between Re$_2$(CO)$_9$(NCMe) and HC$_2$CO$_2$Me, also carried out in refluxing dichloro-

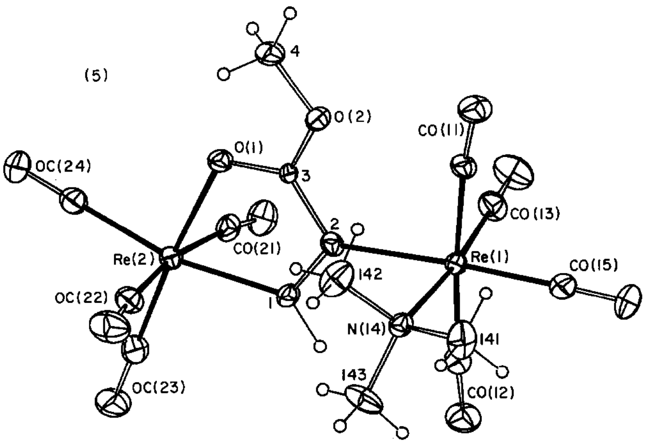

Fig. 2. Plot of a molecule of Re{*C*,*O*-CH=C[Re(CO)$_4$(NMe$_3$)]-C(OMe)O}(CO)$_4$ (**5**). Selected bond distances: Re(1)–C(2) 2.218(9), Re(1)–N(14) 2.31(1), Re(2)–C(1) 2.179(9), Re(2)–O(1) 2.178(6), C(1)–C(2) 1.37(1), C(2)–C(3) 1.44(1), C(3)–O(1) 1.27(1), C(3)–O(2) 1.30(1) Å.

methane, afforded the binuclear complex Re{*C*,*O*-CH=C[Re(CO)$_5$]C(OMe)O}(CO)$_4$ (**4**), described independently during the course of our work by Adams [4]. Our original supposition that this compound was an η^2-alkyne complex led us to treat it with Me$_3$NO in an attempt to induce either addition of the C–H bond across the Re–Re bond (as occurs with HC$_2$Ph [5]) or coordination of the ester carbonyl group. In the event, loss of CO (as CO$_2$) and coordination of NMe$_3$ occurred to give Re{*C*,*O*-CH=C[Re(CO)$_4$(NMe$_3$)]-C(OMe)O}(CO)$_4$ (**5**), as shown by a crystal structure determination.

2.2. Molecular structure of Re{C,O-CH=C[Re(CO)$_4$-(NMe$_3$)]C(OMe)O}(CO)$_4$ (5)

The molecular structure of **5** is shown in Fig. 2; important bond parameters are given in the caption. There are few significant differences between the structures of **4** and **5**, with the exception of the replacement of CO(14) by NMe$_3$ [Re(1)–N 2.31(1) Å]. The CO displaced is that *cis* to the C(2)–Re(1) bond. Adams *et al.* [4] have already discussed the possible mechanism of formation of their complex; in our case, further treatment with Me$_3$NO results in loss of a CO ligand (as CO$_2$) and coordination of NMe$_3$ to the non-chelated Re(1) atom.

3. Experimental details

3.1. General conditions

All reactions were carried out under dry, high purity nitrogen by use of standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm^2) coated with silica gel (Merck 60 GF$_{254}$ 0.5 mm thick).

Instrumentation: IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics. NMR: Bruker ACP300 (^{1}H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz); Bruker CXP300 (^{31}P NMR at 121.49 MHz). FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7kV).

Starting materials: Re$_2$(CO)$_{10}$ (Strem) was used as received. Chemical reagents were laboratory grade and used as received. Re$_2$(CO)$_9$(NCMe) [6], Re$_2$(CO)$_8$-(NCMe)$_2$ [6] and HC$_2$CO$_2$Me [7] were prepared according to the literature procedures.

3.2. Reaction between Re$_2$(CO)$_8$(NCMe)$_2$ and C$_2$Ph$_2$

A solution of Re$_2$(CO)$_8$(NCMe)$_2$ (100 mg, 0.15 mmol) and C$_2$Ph$_2$ (67 mg, 0.38 mmol) in CH$_2$Cl$_2$ (10 ml) was refluxed for 24 h to give an orange solution. The solvent was removed and the residue purified by preparative TLC to give three major bands. The first band (R_f 0.6) was recrystallized from CH$_2$Cl$_2$/hexane to give pure Re$_2$(CO)$_7$(C$_4$Ph$_4$) (**2**) (11 mg, 8%). Anal. Found: C, 45.76; H, 2.52. C$_{35}$H$_{20}$O$_7$Re$_2$ calcd.: C, 45.45; H, 2.16%. IR (hexane): ν(CO) 2087m, 2035vs, 2017s, 1979vs, 1968s, 1938m cm^{-1} (lit.[2]: 2085w, 2035s, 2015m, 1992m, 1979s, 1958w, 1948w cm^{-1}). FAB MS: m/z 924, M$^+$; 896–728, [M − nCO]$^+$ (n = 1–7). The second band (R_f 0.4) (11 mg, 7%) contained Re$_2$(CO)$_5$(C$_4$Ph$_4$)(PhC$_2$Ph) [IR (hexane): ν(CO)

TABLE 2. Crystal data and refinement details for complexes **1** and **5**

Compound	**1**	**5**
Formula	$C_{35}H_{20}Re_2O_7$	$C_{15}H_{13}NO_{10}Re_2$
MW	925.0	739.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.597(2)	7.670(3)
b (Å)	19.80(2)	18.448(3)
c (Å)	16.141(3)	15.200(7)
β (°)	114.34(2)	108.72(4)
U (Å^3)	3085	2037
Z	4	4
D_c (g cm^{-3})	1.99	2.41
F(000)	1744	1360
Crystal size (mm)	0.49 × 0.90 × 0.64	0.51 × 0.21 × 0.17
A^* (min, max)	10.8, 26.9	5.1, 10.5
μ (cm^{-1})	78.9	119
$2\theta_{max}$ (°)	55	50
N	6601	3579
N_o	5422	3059
R	0.039	0.035
R_w	0.045	0.045

2046s, 2018s, 1963(br), 1945(br), 1929(br) cm^{-1} (lit.[2]: 2046s, 2019s, 1967m(br), 1947w(br), 1928m(br) cm^{-1})] and the third band (R_f 0.3) contained $Re_2(CO)_4(C_6Ph_6)(PhC_2Ph)$ (33 mg, 18%) [IR (hexane): ν(CO) 2032s, 1997m, 1962s, 1942w cm^{-1} (lit.[2]: 2035s, 1997m, 1962m, 1942w(br) cm^{-1}].

3.3. *Preparation of Re{C,O-CH=C[Re(CO)$_5$]C-(OMe)O}(CO)$_4$ (4)*

A solution of $Re_2(CO)_9(NCMe)$ (500 mg, 0.75 mmol) was dissolved in CH_2Cl_2 (20 ml) containing methyl propiolate (315 mg, 3.75 mmol) was refluxed for 24 h, during which it became deep orange. The solvent was removed and the resulting solid recrystallized (CH_2Cl_2/MeOH) to give Re{*C*,*O*-CH=C[Re(CO)$_5$]-C(OMe)O}(CO)$_4$ (**4**) as very fine pale yellow needles (315 mg, 60%), m.p. 151–155°C. IR (cyclohexane): ν(CO) 2133w, 2089m, 2022vs, 1990m, 1983s, 1981s, 1935m cm^{-1} (lit.[4]: 2134w, 2090m, 2024s, 1991(sh), 1986(sh), 1982s, 1937s cm^{-1}). ^1H NMR ($CDCl_3$): δ 3.90 (3H, s, OCH_3); 10.42 (1 H, s, C_2H). ^{13}C NMR ($CDCl_3$): δ 54.73 (s, OCH_3); 121.05 (s, HC_2CO_2Me); 127.69 (s, HC_2CO_2Me); 182.01 (s); 182.88 (s); 189.36 (s); 193.02 (s); 193.33 (s, CO); 222.46 (s, CO_2). FAB MS: m/z 708, M^+; 680–484, $[M - nCO]^+$ (n = 1–8).

TABLE 3. Non-hydrogen positional and isotropic displacement parameters, 1

Atom	x	y	z	U_{eq} (Å^2)
Re(1)	0.90588(3)	0.39160(2)	0.65058(2)	0.0350(1)
Re(2)	0.83849(3)	0.29753(2)	0.76183(2)	0.0394(1)
C(11)	1.0276(8)	0.3410(4)	0.6107(6)	0.045(3)
O(11)	1.0948(7)	0.3102(3)	0.5861(5)	0.076(4)
C(12)	0.762(1)	0.3787(5)	0.5299(6)	0.059(4)
O(12)	0.6778(8)	0.3710(5)	0.4588(5)	0.099(4)
C(13)	0.9487(8)	0.4711(4)	0.6030(5)	0.045(3)
O(13)	0.9674(7)	0.5212(3)	0.5735(4)	0.065(3)
C(21)	0.931(1)	0.2147(4)	0.8223(7)	0.065(5)
O(21)	0.9846(9)	0.1659(4)	0.8586(6)	0.108(5)
C(22)	0.6528(9)	0.2617(5)	0.7277(6)	0.057(4)
O(22)	0.5437(7)	0.2416(4)	0.7086(6)	0.096(4)
C(23)	0.843(1)	0.3312(5)	0.8790(6)	0.064(4)
O(23)	0.843(1)	0.3538(4)	0.9439(5)	0.107(5)
C(24)	0.830(1)	0.2537(5)	0.6506(6)	0.064(4)
O(24)	0.821(1)	0.2196(4)	0.5906(6)	0.098(5)
C(1)	0.7639(8)	0.4017(4)	0.7218(5)	0.037(3)
C(101)	0.6128(8)	0.4176(4)	0.6884(5)	0.041(3)
C(102)	0.5141(9)	0.3962(5)	0.6070(6)	0.057(4)
C(103)	0.3773(9)	0.4123(6)	0.5793(7)	0.067(4)
C(104)	0.3348(9)	0.4483(6)	0.6323(8)	0.073(5)
C(105)	0.428(1)	0.4692(6)	0.7161(8)	0.078(6)
C(106)	0.5677(9)	0.4537(5)	0.7443(6)	0.058(4)
C(2)	0.8634(7)	0.4524(4)	0.7594(5)	0.035(3)
C(201)	0.8301(7)	0.5254(4)	0.7602(5)	0.039(3)
C(202)	0.8744(8)	0.5600(4)	0.8413(6)	0.048(3)
C(203)	0.836(1)	0.6264(5)	0.8424(7)	0.068(5)
C(204)	0.753(1)	0.6594(5)	0.7645(8)	0.072(5)
C(205)	0.707(1)	0.6250(5)	0.6834(7)	0.068(5)
C(206)	0.7458(9)	0.5591(4)	0.6795(6)	0.050(4)
C(3)	1.0083(7)	0.4281(4)	0.8020(5)	0.034(3)
C(301)	1.1262(7)	0.476294)	0.8484(5)	0.036(3)
C(302)	1.2042(9)	0.4675(5)	0.9411(6)	0.057(4)
C(303)	1.314(1)	0.5101(5)	0.9876(7)	0.070(4)
C(304)	1.348(1)	0.5615(5)	0.9442(9)	0.087(6)
C(305)	1.271(1)	0.5710(5)	0.8536(8)	0.071(5)
C(306)	1.1583(9)	0.5294(4)	0.8059(6)	0.052(4)
C(4)	1.0275(7)	0.3591(4)	0.8008(5)	0.038(3)
C(401)	1.1702(8)	0.3316(4)	0.8453(5)	0.040(3)
C(402)	1.2083(9)	0.2942(4)	0.9231(6)	0.059(4)
C(403)	1.342(1)	0.2721(5)	0.9713(7)	0.078(5)
C(404)	1.440(1)	0.2857(5)	0.9388(9)	0.090(5)
C(405)	1.4052(9)	0.3235(5)	0.8612(8)	0.073(5)
C(406)	1.2719(9)	0.3447(4)	0.8144(6)	0.056(4)

TABLE 4. Non-hydrogen positional and isotropic displacement parameters, 5

Atom	x	y	z	U_{eq} (Å^2)
Re(1)	0.29071(5)	0.31553(2)	0.50144(3)	0.0350(2)
C(11)	0.076(2)	0.2956(5)	0.3897(7)	0.047(4)
O(11)	−0.040(1)	0.2891(4)	0.3208(6)	0.072(4)
C(12)	0.503(2)	0.3440(6)	0.6101(8)	0.049(4)
O(12)	0.625(1)	0.3646(5)	0.6703(6)	0.078(4)
C(13)	0.451(2)	0.3034(6)	0.4268(9)	0.059(5)
O(13)	0.545(1)	0.2956(6)	0.3837(7)	0.088(5)
N(14)	0.094(1)	0.3186(4)	0.5892(6)	0.041(3)
C(141)	−0.013(2)	0.3859(6)	0.570(1)	0.078(7)
C(142)	−0.036(2)	0.2562(7)	0.569(1)	0.076(6)
C(143)	0.198(2)	0.3149(8)	0.6900(8)	0.079(6)
C(15)	0.262(2)	0.4171(6)	0.4693(8)	0.054(5)
O(15)	0.260(1)	0.4786(4)	0.4521(7)	0.084(5)
Re(2)	0.50020(6)	0.06043(2)	0.64787(3)	0.0409(2)
C(21)	0.705(2)	0.0730(5)	0.5934(8)	0.049(4)
O(21)	0.826(1)	0.0848(5)	0.5692(7)	0.074(4)
C(22)	0.308(2)	0.0644(6)	0.7082(8)	0.058(5)
O(22)	0.201(2)	0.0716(6)	0.7440(7)	0.094(5)
C(23)	0.680(2)	0.0583(6)	0.7691(9)	0.061(5)
O(23)	0.788(1)	0.0559(5)	0.8400(6)	0.092(4)
C(24)	0.494(2)	−0.0462(6)	0.6383(8)	0.056(5)
O(24)	0.490(1)	−0.1074(4)	0.6315(6)	0.074(4)
C(1)	0.467(2)	0.1771(5)	0.6266(7)	0.046(4)
C(2)	0.340(1)	0.2008(5)	0.5459(7)	0.038(3)
C(3)	0.244(1)	0.1401(4)	0.4918(6)	0.031(3)
O(1)	0.2837(9)	0.0745(3)	0.5151(4)	0.042(2)
O(2)	0.1083(9)	0.1515(3)	0.4159(5)	0.045(3)
C(4)	0.005(2)	0.0905(6)	0.3700(8)	0.061(5)

3.4. *Reaction between Re{C,O-CH=C[Re(CO)$_5$]-C(OMe)O}(CO)$_4$ (4) and Me$_3$NO*

Me_3NO (10.6 mg, 0.14 mmol) was added in portions to a stirred solution of **4** (100 mg, 0.14 mmol) in CH_2Cl_2 (10 ml). The solvent was removed and the yellow-green residue purified by preparative TLC (10 : 3 light petroleum/acetone) to give three bands. The top band (R_f 0.6) was $Re_2(CO)_9(HC_2CO_2Me)$ (18 mg). The second band (R_f 0.3) was recrystallized (CH_2Cl_2/hexane) to give lime green crystals of Re{*C*,*O*-

CH=C[Re(CO)$_4$(NMe$_3$)]C(OMe)O}(CO)$_4$ (**5**) (39 mg, 38%), m.p. 129–132°C. Anal. Found: C, 24.43; H, 1.77; N, 1.91%. $C_{15}H_{13}NO_{10}Re_2$ calcd.: C, 24.36; H, 1.76; N, 1.89%. IR (THF): ν(CO) 2092w, 2081m, 1982(br), 1969(sh), 1924s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.85 (9H, s, NMe$_3$); 3.92 (3H, s, OMe); 10.56 (1H, s, C$_2$H). ^{13}C NMR (CDCl$_3$): δ 54.21 (s, OMe); 59.98 (s, NMe$_3$); 189.87 (s); 190.16 (s); 191.27 (s); 191.98 (s); 193.67 (s, CO); 217.11 (s, CO$_2$Me). FAB MS; m/z 739, M$^+$; 711–571, [M $-$ nCO]$^+$ ($n = 1$–6). The lower band (R_f 0.2) (7 mg) was not characterized.

3.5. *Crystallography*

Unique diffractometer data sets were measured with the specified $2\theta_{max}$ limits at *ca.* 295 K (2θ–θ scan mode; monochromatic Mo Kα radiation, λ 0.71073 Å) yielding N independent reflections; N_o with $I > 3\sigma(I)$ were considered observed and used in the full matrix least squares refinements after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values, the ligand hydrogen of **5** being confirmed in a difference map. Conventional residuals, R, R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed, computed using the XTAL 3.0 program system [8] implemented by S.R. Hall. Pertinent results are given in the figures and tables.

Supplementary data have been deposited with the Cambridge Crystallographic Data Centre.

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