Neutral, Acetate-bridged, Binuclear Alkyls of Rhenium(III) †

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The binuclear methyl compound $Re_2Me_2(O_2CMe)_4$ is obtained from the interaction of dilithium octamethyldirhenate(III), $Li_2Re_2Me_8\cdot 2Et_2O$, with acetic acid. Other neutral, acetate-bridged, binuclear alkyls of stoicheiometry $Re_2R_4(O_2CMe)_2$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, and CH_2Ph) are obtained from the interaction of the dialkylmagnesiums, R_2Mg, with tetra-acetatodichlorodirhenium(III), $Re_2(O_2CMe)_4Cl_2$, in diethyl ether.

The compounds which evidently contain strong rhenium–rhenium quadruple bonds have been characterised by i.r. and n.m.r. spectroscopy (^{1}H and ^{13}C{^{1}H}). The results of structure determinations by *X*-ray crystallography are also reported briefly.

THE interaction of the binuclear transition-metal acetates of chromium(II), molybdenum(II), ruthenium(II,III) and rhodium(II), which contain metal–metal multiple bonds, with dialkylmagnesiums in the presence of PMe_3 has been reported.[1,2]

TABLE 1

^{1}H and ^{13}C{^{1}H} N.m.r. data for $Re_2R_4(O_2CMe)_2$ compounds

Compound	^{1}H n.m.r. (δ) [a]	Assignment	^{13}C{^{1}H} n.m.r.[b]
(E) $Re_2(CH_2SiMe_3)_4(O_2CMe)_2$	2.50s(6)	μ-$\mathrm{O_2C}\mathit{Me}$	22.36s
	1.84s(8)	$\mathrm{Re}\mathit{CH_2}\mathrm{SiMe_3}$	33.70s
	0.30s(36)	$\mathrm{ReCH_2Si}\mathit{Me_3}$	3.57s
		μ-$\mathrm{O_2}\mathit{C}\mathrm{Me}$	187.19s
(F) $Re_2(CH_2CMe_3)_4(O_2CMe)_2$	2.52s(6)	μ-$\mathrm{O_2C}\mathit{Me}$	21.76s
	2.71s(8)	$\mathrm{Re}\mathit{CH_2}\mathrm{CMe_3}$	60.49s
	1.32s(36)	$\mathrm{ReCH_2C}\mathit{Me_3}$	35.15s
		$\mathrm{ReCH_2}\mathit{C}\mathrm{Me_3}$	35.95s
		μ-$\mathrm{O_2}\mathit{C}\mathrm{Me}$	186.76s
(G) $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$	2.27s(6)	μ-$\mathrm{O_2C}\mathit{Me}$	21.58s [c]
	2.85s(8)	$\mathrm{Re}\mathit{CH_2}\mathrm{CMe_2Ph}$	59.15s
	1.40s(24)	$\mathrm{ReCH_2C}\mathit{Me_2}\mathrm{Ph}$	32.92s
	7.1—7.7br(20)	$\mathrm{ReCH_2CMe_2}\mathit{Ph}$	125.05s
			125.89s
			127.90s
			153.91s
		$\mathrm{ReCH_2}\mathit{C}\mathrm{Me_2Ph}$	41.36s
		μ-$\mathrm{O_2}\mathit{C}\mathrm{Me}$	185.81s
(H) $Re_2(CH_2Ph)_4(O_2CMe)_2$	2.71(6) [d]	μ-$\mathrm{O_2C}\mathit{Me}$	21.49s [c]
	3.33s(8)	Re-$\mathit{CH_2}\mathrm{Ph}$	40.36s
	6.5—7.3br(20)	Re-$\mathrm{CH_2}\mathit{Ph}$	123.90
			128.08
			129.76
			142.78
		μ-$\mathrm{O_2}\mathit{C}\mathrm{Me}$	187.39

[a] Benzene solvent and internal reference (δ 7.27) and referenced to $SiMe_4$ (δ 0.0) at 60 MHz and 35 °C. Relative intensity in parentheses. [b] [$^2H_6$]Benzene solvent and internal reference (δ 128.7) and referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz. Peaks to high frequency (low field) of $SiMe_4$ are positive. [c] [$^2H_3$]Chloroform, solvent and internal reference (δ 76.9) and referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz. [d] [^{2}H]Chloroform solvent with $SiMe_4$ (δ 0.0) as internal reference.

With $Re_2(O_2CMe)_4Cl_2$ in the absence of phosphine the use of dialkylmagnesiums gives neutral, binuclear, crystalline alkyls which still retain acetate and the metal–metal quadruple bond.

A binuclear, acetate-bridged, methyl compound has also been obtained from $Li_2Re_2Me_8\cdot 2Et_2O$ and acetic acid. Several derivatives containing the '$Re_2Me_2(O_2CMe)_2$' unit are also described.

For the new compounds spectroscopic data are given in Table 1 and analytical data in Table 2.

Methyl Compounds.—(a) *Di-μ-acetato-bis*[*acetato*(*methyl*)*rhenium*(III)](Re-Re).· This bright red, air-stable, crystalline compound, (A), can be isolated in *ca.* 50% yield from the interaction of solid $Li_2Re_2Me_8\cdot 2Et_2O$ and an excess of acetic acid. The structure of the compound, (1), has recently been determined by *X*-ray diffraction;[3] two acetate groups bridge two rhenium atoms linked by a short metal–metal bond while each metal holds an unsymmetrical chelate acetate and a methyl group. The latter are *trans* to each other with respect to the Re–Re axis and each rhenium atom has a roughly

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† No reprints available.

[1] R. A. Andersen, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J.C.S. Chem. Comm.*, 1977, 283; *J.C.S. Chem. Comm.*, 1977, 865.

[2] R. A. Andersen, R. A. Jones, and G. Wilkinson, *J.C.S. Dalton*, 1978, 446.

[3] K. M. A. Malik and M. B. Hursthouse, *J.C.S. Dalton*, 1978, in the press.

octahedral environment. A structure of this type has not been previously reported for binuclear multiply bonded transition-metal acetates.[4] The bond distances suggest that the Re–CH_3 groups are strongly bound while the oxygen atoms of the chelating acetates occupying the co-ordination sites along the Re–Re axis are weakly bound.[3] The i.r. spectrum contains a strong absorption at 1 555 cm^{-1} (ν_{CO}) which is probably due to the asymmetric bidentate acetate group. This band is not found in the spectra of derivatives of (A) which appear to contain only the symmetrical bridging acetates and these have lower C–O stretching frequencies. The ^1H n.m.r. spectrum consists of three equal peaks indicating that the structure in solution is similar to that in the solid state.

TABLE 2

Analytical data

Compound	Colour	M.p.[b] (θ_c/°C)	Found C(%)	Found H(%)	Found Re(%)	Found *M* [a]	Required C(%)	Required H(%)	Required Re(%)	Required *M*
(A) $Re_2Me_2(O_2CMe)_4$	Red	200 250 d *	19.1	2.9		720	18.8	2.8		638
(B) $\{ReMe(O_2CMe)Cl\}_n$	Purple	260—270 d	12.5	2.0	12.7 [c]		12.2	2.0	12.0 [c]	
(C) $Re_2Me_2(O_2CMe)_2Cl_2{\cdot}Me_2SO$	Red	260—270 d	15.0	2.9	10.0 [c]		14.3	2.7	10.6 [c]	
(D) $\{ReMe(OMe)(O_2CMe)\}_n$	Mauve	100—120 d	17.0	3.3	63.5		16.5	3.2	63.9	
(E) $Re_2(CH_2SiMe_3)_4(O_2CMe)_2$	Red	135—137	29.3	6.3		877	28.6	6.0		838
(F) $Re_2(CH_2CMe_3)_4(O_2CMe)_2$	Red	158—160	37.3	6.6	47.6	680	37.2	6.5	48.1	774
(G) $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$	Red	178—180	50.5	5.6	34.6	950	49.7	5.5	35.0	1 062
(H) $Re_2(CH_2Ph)_4(O_2CMe)_2$	Purple	156—158	44.2	4.2			45.0	4.0		

* d = decomposed. [a] Cryoscopically in benzene. [b] Many of the compounds decompose gradually over a wide range of temperature. [c] Chlorine.

(b) *Other methyl compounds.* In dichloromethane (A) reacts with chlorine gas to give a purple powder of stoicheiometry $\{ReMe(O_2CMe)Cl\}_n$, (B). This compound is insoluble in most solvents although red, air stable crystals of stoicheiometry $Re_2Me_2(O_2CMe)_2Cl_2{\cdot}Me_2SO$ (C) can be obtained from dimethyl sulphoxide. The structure of (B) is probably polymeric with chlorine atoms bridging the $[Re_2Me_2(O_2CMe)_2]$ units (2) since the *X*-ray crystal structure of (C) [3] shows that this retains the '$Re_2(O_2CMe)_2Me_2$' unit with the methyl groups *trans* with respect to Re–Re (3). One molecule of dimethyl sulphoxide is bound to one end of the molecule *via* its oxygen atom [5] (ν_{SO} = 935 cm^{-1}) while no corresponding ligand is found at the other end of the molecule. The basic structure is quite similar to those of the binuclear mixed halogeno-acetates of rhenium(III).[6]

Compounds of formula $Li_2Re_2Me_{(8-x)}Cl_x$ are probably formed when insufficient methyl-lithium is used in the preparation of $Li_2Re_2Me_8{\cdot}2Et_2O$. The action of glacial acetic acid on these solutions (see Experimental section) results in the formation of an insoluble purple material which still retains chlorine. Microanalytical data were not reproducible and we have been unable to purify it by other means. However, with dimethyl sulphoxide this material yields red crystals of (C). The mixed methyl-chloro-species which are produced are probably similar to those of tungsten in $Li_4W_2(Me)_{8-x}Cl_x{\cdot}4thf$.[7]

On warming (A) in methanol a mauve insoluble powder of stoicheiometry $\{ReMe(OMe)(O_2CMe)\}_n$ (D) is formed. The i.r. spectrum (ν_{CO} = 1 025 cm^{-1}) indicates the presence of a methoxide.[8] The structure might be similar to that of (B) but with methoxide bridges [9] instead of chlorine bridges.

Di-μ-acetato-bis[dialkylrhenium(III)] *Compounds.—Trimethylsilylmethyl and neopentyl.* Deep red, air-stable crystals of $Re_2R_4(O_2CMe)_2$ [R = CH_2SiMe_3 (E) or CH_2CMe_3 (F)] are obtained in high yield from the interaction of $Re_2(O_2CMe)_4Cl_2$ and the corresponding dialkylmagnesium in diethyl ether. The compounds are isostructural (4) on the basis of n.m.r. and molecular-weight data. Two rhenium atoms, retaining the metal–metal bond, are bridged by two acetate units and two alkyl groups are bonded to each rhenium(III) atom. The ^1H n.m.r. spectra consist of three singlets (relative areas 3 : 4 : 18) indicating that all four alkyl groups are chemically equivalent.

The use of a large excess of the dialkylmagnesium merely results in the more rapid formation of (E) or (F); no products can be isolated using lithium alkyls.

The compounds are quite soluble in dichloromethane, methanol, and acetone as well as hydrocarbon solvents, without decomposition for several weeks. They do not react with H_2, CO, or C_2H_4 under ambient conditions (1 atm and room temperature). With NO, in light petroleum, red–brown solutions are obtained although we have not isolated any pure compounds.

2-Methyl-2-phenylpropyl. The 2-methyl-2-phenylpropyl analogue of (E) and (F), $Re_2(CH_2CMe_2Ph)_4(O_2CMe)_2$, (G), is insoluble in light petroleum and only moderately soluble in benzene. However it is quite soluble in chloroform and can be recrystallised from dichloromethane as red prisms. N.m.r. data (Table 1) show that it is isostructural with (E) and (F) although it survives in air only for days instead of weeks.

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[4] F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27.

[5] W. Kitching, C. J. Moore, and D. Doddrell, *Inorg. Chem.*, 1970, **9**, 541, and references therein.

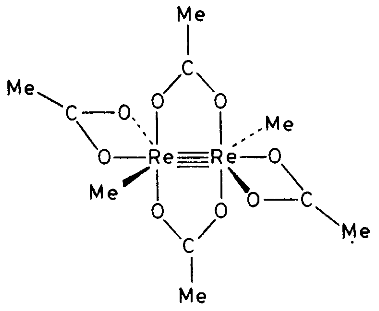
[6] F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, 1966, **5**, 1798.

[7] F. A. Cotton, S. Koch, K. Mertis, M. Millar, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1977, **99**, 4989.

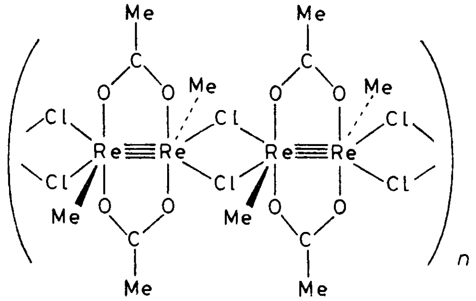
[8] D. M. Adams, 'Metal Ligand and Related Vibrations', E. Arnold, London, 1967.

[9] D. C. Bradley, *Progr. Inorg. Chem.*, 1960, **2**, 303; *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.

Benzyl. The benzyl compound, $Re_2(CH_2Ph)_4(O_2CMe)_2$, (H), is formed quite rapidly (*ca.* 15 min) in high yield under similar conditions to those described above for the other alkyls. It can only be handled briefly in air and is insoluble in hydrocarbon solvents. However, it may be obtained as purple crystals from diethyl ether and survives sufficiently long enough in $CDCl_3$ for n.m.r. data to be obtained.



(1)



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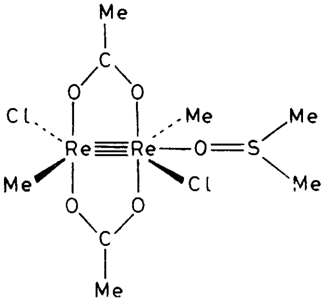
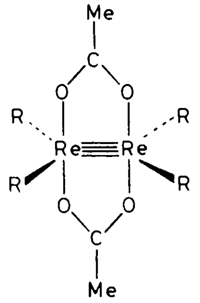


(3)



(4)

R = CH_2SiMe_3
CH_2CMe_3
CH_2CMe_2Ph
CH_2Ph

Molecular-weight measurements were not made due to its insolubility in hydrocarbons and air sensitivity, though the n.m.r. data suggest that it is isostructural with (E), (F), and (G).

The interaction of $Re_2(O_2CMe)_4Cl_2$ and the dialkylmagnesiums in the presence of an excess of PMe_3 results in low yields of materials which we have not attempted to characterize fully.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn), and by Imperial College laboratories. Spectrometers; Perkin-Elmer R12 (^1H); Varian XL-100 ($^{13}C\{^1H\}$ F.T.); Perkin-Elmer PE 457, 257 (i.r.).

All operations were carried out under nitrogen or *in vacuo.* The diethyl ether, tetrahydrofuran, and light petroleum were dried over sodium and distilled under nitrogen before use. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Light petroleum used had b.p. 40—60 °C. M.p.s were determined in sealed capillaries under nitrogen. The yields of (B), (C), and (D) were all quantitative.

(A) *Di-μ-acetato-bis[acetato(methyl)rhenium*(III)](Re–Re).—A deoxygenated mixture of glacial acetic acid (35 cm^3) and acetic anhydride (5 cm^3) was added to solid $Li_2Re_2Me_8 \cdot 2Et_2O$, at −196 °C, obtained from rhenium pentachloride (6.04 g, 16.7 mmol) and methyl-lithium (125 cm^3 of a 1.0M-diethyl ether solution, 0.125 mol) as previously described.[10] The mixture was allowed to warm slowly to room temperature (over 10 h) after which distilled water (50 cm^3) was added to it. The red-brown slurry was stirred (2 h) and filtered on a sintered glass frit. The residue was extracted into dichloromethane (10 × 20 cm^3) and the extracts filtered; the filtrates were collected and the solvent removed under vacuum. The pink residue was recrystallised from boiling glacial acetic acid to give red *prisms*; yield 2.0 g (38% based on $ReCl_5$). [*Note*: the yield of $Li_2Re_2Me_8 \cdot 2Et_2O$ from $ReCl_5$ is only *ca.* 50%.[10]] The compound does not have a sharp melting point but decomposes over the range 200—250 °C. I.r. (Nujol) ν/cm^{-1}: 1 555s, 1 450s,br, 1 395s, 1 375s, 1 365s, 1 352s, 1 342s, 1 155w, 1 045m, 1 010m, 934m, 692s, 676s, 638w, 617w, 545m, 540m, 480w, 372m, 339m, 332w, 305w, and 289m. ^1H n.m.r. ($CDCl_3$) δ 3.23s(6), 2.35s(6), and 1.80s(6).

The compound is moderately soluble in CH_2Cl_2, $CHCl_3$, and C_6H_6 but virtually insoluble in acetone, CS_2, and tetrahydrofuran. It decomposes both in pyridine and tetramethylethylenediamine to give green-brown materials, and also when warmed in ethanol, water, dimethyl sulphoxide, dimethylformamide, and ammonia (*d* 0.880) to give red-brown solutions. The action of MeSH and H_2S on CH_2Cl_2 solutions also results in decomposition. It does not react with CO, H_2, ethylene, or SO_2 under ambient conditions (1 atm, room temp.) and appears to be indefinitely air-stable.

(B) *Di-μ-acetato-bis[chloro(methyl)rhenium*(III)] (B) *and its Dimethyl Sulphoxide Adduct* (C).—Chlorine gas was passed slowly through a solution of complex (A) (0.1 g, 0.16 mmol) in dichloromethane (15 cm^3) for 5 min. The purple powder was collected, washed with diethyl ether (2 × 5 cm^3), and dried *in vacuo.* I.r. (Nujol) ν/cm^{-1}: 1 470s, 1 450s, 1 385s, 1 370m, 1 350m, 1 210w, 1 170w, 1 035m, 1 025m, 735m, 680s, 630w, 530m, 380m, 340m, 305w, 295m, and 280m.

Red crystals of the dimethyl sulphoxide *adduct* $Re_2Me_2Cl_2(O_2CMe)_2 \cdot Me_2SO$ (C), were obtained from complex (B) (0.1 g, 0.016 mmol) warmed in dimethyl sulphoxide (2 cm^3) after several days at room temperature. They were collected, washed with acetone (2 × 0.5 cm^3), and dried *in vacuo.* I.r. (Nujol) ν/cm^{-1}: 1 465s,br, 1 440s,br, 1 400s,br, 1 375s,

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[10] F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shive, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1976, **98**, 6922.

1 365s, 1 350m, 1 340m, 1 310w, 1 290w, 1 210w, 1 192w, 1 020m, 983s, 945s, 931s, 717w, 675s, 627w, 545m, 530w, 405m, 395w, 375w, 368m, 350w, 335m, 325w, 291m, 289m, 280w, and 265w.

Complex (C) was also prepared as follows. A deoxygenated mixture of glacial acetic acid (4 cm^3) and acetic anhydride (0.5 cm^3) was added to a solution of $Li_2Re_2Me_8$ in diethyl ether, prepared from rhenium pentachloride (1.28 g) and methyl-lithium (6 mol equiv.) (as above) at −50 °C. The stirred solution was allowed to warm to room temperature and evaporated to dryness *in vacuo*. The residue was washed with dichloromethane (150 cm^3) and collected. The material is insoluble in most solvents and could not be purified by crystallisation or other means. However, with dimethyl sulphoxide crystals of (C) were obtained after several days at room temperature.

catena-μ-*Acetato-methoxy(methyl)rhenium*(III) (D).—Complex (A) (0.1 g, 1.6 mmol) was warmed (50 °C) in methanol (25 cm^3) for 5 min. The mauve powder was filtered off, washed with diethyl ether, and dried *in vacuo*. I.r. (Nujol) ν/cm^{-1}: 1 490m, 1 445s, 1 405s, 1 360m, 1 350m, 1 040w, 1 020s, 750w, 720w, 675s, and 630w.

Di-μ-acetato-bis[bis(trimethylsilylmethyl)rhenium(III)] (E).—Bis(trimethylsilylmethyl)magnesium (1.4 cm^3 of a 1.0M-diethyl ether solution, 1.4 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.32 g, 0.47 mmol) suspended in diethyl ether (30 cm^3). After the mixture had been stirred for 10 h the solvent was evaporated and the red-brown residue extracted into light petroleum (50 cm^3). The solution was filtered and evaporated to *ca.* 5 cm^3 and cooled (−20 °C). The red *needles* were collected and dried *in vacuo*; yield 0.2 g (51%). I.r. (Nujol) ν/cm^{-1}: 1 357w, 1 335w, 1 260s, 1 245s, 980m, 940m, 910w, 850s, 825s, 745m, 725m, 705m, 680m, and 673s.

Di-μ-acetato-bis[bis(2,2-dimethylpropyl)rhenium(III)].—Bis(2,2-dimethylpropyl)magnesium (5.7 cm^3 of a 0.61M-diethyl ether solution, 3.48 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.79 g, 1.16 mmol) in diethyl ether (50 cm^3) at 0 °C. The mixture was stirred (10 h) at room temperature and then evaporated to dryness; the residue was then extracted into light petroleum (50 cm^3) and filtered. The filtrate was concentrated (20 cm^3), refiltered, and cooled (−20 °C) to yield deep red *crystals*. These were washed with cold, light petroleum (2 × 1 cm^3) and dried *in vacuo*; yield 0.5 g, (45%). I.r. (Nujol) ν/cm^{-1}: 1 465s,br, 1 435s,br, 1 420s, 1 375s, 1 360s, 1 350s, 1 345s, 1 265w, 1 227s, 1 105w, 1 030w, 1 005w, 920w, 742m, 735m, 720w, 705w, 664s, 620m, 585m, and 560s.

Di-μ-acetato-bis[bis(2-methyl-2-phenylpropyl)rhenium(III)] (G).—Bis(2-methyl-2-phenylpropyl)magnesium (3.4 cm^3 of a 1.0M-diethyl ether solution, 3.4 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.76 g, 1.1 mmol) in diethyl ether (75 cm^3) at −78 °C. The suspension was stirred and allowed to warm slowly to room temperature (10 h); it was then stirred for an extra 24 h. The mixture was evaporated to dryness and washed with light petroleum (50 cm^3). The remaining pink residue was dried *in vacuo* and extracted into dichloromethane (60 cm^3). The solution was filtered and evaporated to *ca.* 15 cm^3 under reduced pressure. A pink powder was deposited which was redissolved by warming the solution briefly to *ca.* 50 °C. Cooling (−20 °C) yielded red *prisms*. They were washed with light petroleum (5 cm^3) and dried *in vacuo*; yield 0.4 g (34%). I.r. (Nujol) ν/cm^{-1}: 3 080w, 3 050w, 3 020w, 1 595w, 1 493m, 1 465s,br, 1 455s,br, 1 435s, 1 420m, 1 405w, 1 375s, 1 360m, 1 350m, 1 275w, 1 190m, 1 025w, 765s, 700s, 667s, 625m, and 585m.

Di-μ-acetato-bis[di(benzyl)rhenium(III)] (H).—Dibenzylmagnesium (1.0 cm^3 of a 0.94M-diethyl ether solution, 0.94 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.24 g, 0.35 mmol) in diethyl ether (40 cm^3) at −78 °C. The suspension was warmed to 0 °C and stirred at room temperature for 20 min. The solution was filtered and evaporated to dryness. The residue was extracted into diethyl ether (30 cm^3) and filtered. The filtrate was evaporated to *ca.* 15 cm^3 and cooled (−20 °C) to yield dark purple *crystals*; yield 0.15 g (50%). I.r. (Nujol) ν/cm^{-1}: 3 070w, 3 050w, 3 010w, 1 590m, 1 485m, 1 465s,br, 1 455s,br, 1 445s, 1 375s, 1 365m, 1 350m, 1 260w, 1 207m, 1 197,w 1 175w, 1 025w, 800w, 755s, 745m, 720w, 700s, 667s, and 625w.

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