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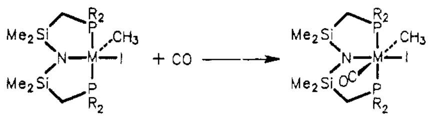
particular square-pyramidal geometry observed in the solid state, i.e., sqpl, persists in solution; in other words, carbon monoxide adds to the open face of the square pyramid trans to the apical methyl ligand (eq 6). The stereoselectivity of the CO addition also tends to exclude the possibility that the five-coordinate methyl halides are involved in stereochemical rearrangements on the NMR time scale as this should lead to the formation of isomeric octahedral[33] carbonyl derivatives.



(6)

sqpl ol

Notable in these carbonylation reactions of the rhodium and iridium methyl iodides is the absence of any products corresponding to migratory insertion, i.e., acetylmetal complexes. We attribute this to both the unfavorable trans disposition of the methyl and carbonyl ligands in the ol isomer and the presence of the strongly bound tridentate ligand. This contrasts the behavior[26] of $Rh(CH_3)I_2(PPh_3)_2$ with carbon monoxide for which two isomeric forms of the octahedral acetyl complex $Rh(COCH_3)I_2(PPh_3)_2CO$ are reported.

Conclusions

Amide complexes of rhodium and iridium in both the formal +1 and +3 oxidation levels have now been realized. Undoubtedly, the facility by which these complexes are formed and their resultant stability are due to the incorporation of the amide donor into a chelating array that contains phosphine donors.

The presence of the amide ligand in the coordination sphere does not preclude simple substitution reactions of the corresponding square-planar d^8 derivatives (Rh(I) and Ir(I)), nor does it impede the oxidative addition of certain methyl halides to generate five-coordinate d^6 complexes (Rh(III) and Ir(III)); as both of these types of transformations are part of the arsenal of the synthetic coordination chemist, it would appear that the design of transition-metal-based catalytic systems using amide ancillary ligands is at least viable.

Acknowledgment. Financial support was generously provided by NSERC of Canada and the Alfred P. Sloan Foundation. We also thank Professor James Trotter for the use of his diffractometer and structure solving programs. The generous loan of $RhCl_3$ and $IrCl_3$ from Johnson-Matthey is also acknowledged.

Registry No. **1**, 84074-26-0; **2**, 84074-27-1; **3**, 84074-25-9; **4**, 84074-29-3; **5**, 84074-28-2; **6**, 84074-30-6; **7**, 104835-44-1; **8**, 84074-31-7; **9**, 104835-43-0; **10**, 84074-32-8; **11**, 104835-45-2; **12**, 96110-15-5; **13**, 104848-75-1; **14**, 96110-11-1; **15**, 104835-46-3; **16**, 96110-12-2; **17**, 104835-47-4; **18**, 104293-28-9; **19**, 104835-48-5; **20**, 104835-49-6; **21**, 104835-50-9; **22**, 104835-51-0; **23**, 104874-24-0; $[Rh(\eta^2\text{-}C_8H_{14})_2Cl]_2$, 12279-09-3; $[Ir(\eta^2\text{-}C_8H_{14})_2Cl]_2$, 12246-51-4; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$, 12081-16-2; $Rh(PMe_3)_4Cl$, 70525-09-6; $Rh(PPh_3)_3Cl$, 14694-95-2; $LiN(SiMe_2CH_2P(i\text{-}Pr)_2)_2$, 94372-12-0; $LiN(SiMe_2CH_2PPh_2)_2$, 77617-69-7.

Supplementary Material Available: Tables of intraannular torsion angles and hydrogen coordinates and isotropic thermal parameters (3 pages); a listing of observed and calculated structure factors (19 pages); ordering information is given on any current masthead page.

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[33] Kinetically trapping the various five-coordinate isomers by CO would lead to substitutionally inert and configurationally stable derivatives which would be easily distinguished.

The Rhenium Mesityl Oxide Complex (η^5-C_5Me_5)Re(CO)$_2$(η^2-$Me_2C{=}CHCOMe$): X-ray Crystal Structure Determination and Solution Isomerism

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Received April 14, 1986

Reaction of $Cp^*Re(CO)_2(N_2)$ ($Cp^* = \eta\text{-}C_5Me_5$) with $[Me_3O][BF_4]$ or $[Et_3O][BF_4]$ in acetone affords $Cp^*Re(CO)_2(\eta^2\text{-}Me_2C{=}CHCOMe)$ (**8**), which is also obtainable from $Cp^*Re(CO)_2(THF)$ (THF = tetrahydrofuran) and mesityl oxide. The X-ray crystal structure of **8** shows the mesityl oxide to be coordinated through the olefinic group and to be in the s-cis conformation. Compound **8** crystallizes in the space group $P2_1/n$ with $a = 8.515$ (2) Å, $b = 14.277$ (4) Å, $c = 15.093$ (4) Å, and $\beta = 99.30$ (2)°. The structure was solved by using 1885 observed reflections with intensities $I \geq 3\sigma(I)$ in the range $0° \leq 2\theta \leq 48°$ and refined to values of $R = 0.034$ and $R_w = 0.044$. The presence, in solution, of s-cis and s-trans conformers of **8** is indicated by two sets of ν(CO) absorptions in the IR spectrum (hexane), but the single set of ^1H NMR resonances observed over the temperature range +50 to −80 °C indicates these conformers to be in rapid equilibrium.

Introduction

Reports of transition-metal complexes of mesityl oxide (4-methyl-3-penten-2-one) (**1**) date back to 1840, when Zeise[1] described the platinum complex $C_6H_{10}OPtCl_2$. More than a century later, Parshall and Wilkinson[2] used IR and ^1H NMR results to formulate this platinum compound as a polymer, with $PtCl_2$ units bridged by the mesityl oxide ligand (**1**) using both its olefin and ketone functions. However, much more recently Gillard et al.[3] have reexa-

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(1) (a) Zeise, H. *J. Prakt. Chem.* **1840**, *20*, 193. (b) Prandtl, W.; Hofmann, K. A. *Chem. Ber.* **1900**, *33*, 2981.

(2) Parshall, G. W.; Wilkinson, G. *Inorg. Chem.* **1962**, *1*, 896.

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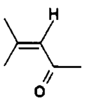
mined the NMR spectrum and have reformulated this complex not to contain mesityl oxide, but its unconjugated isomer 4-methyl-4-penten-2-one (**2**) instead. Besides isomerization, another process that can occur in complexation reactions of mesityl oxide is facile deprotonation. For example, Parshall and Wilkinson[2] have formulated the compound prepared from $PdCl_2$ and mesityl oxide as the π-allyl complex **3** containing the deprotonated form **4** of mesityl oxide, i.e., 2,4-dimethyl-1-oxapentadienyl. A more recent example is the reaction of mesityl oxide with $[Cp^*Ir(acetone)_3]^{2+}$ to form complex **5** in which the deprotonated ligand **4** now acts as an η^5 ligand.[4] Furthermore, **4** can be complexed in its enol form, 2-hydroxy-4-methylpentadienyl (**6**), as occurs[4] in the related iridium complex **7**. It is evident that none of the above compounds, even though synthesized from mesityl oxide, actually contains an authentic, unmodified, mesityl oxide molecule as a ligand. Consequently, the authenticity of mesityl oxide complexes that have been assumed to contain the mesityl oxide ligand (**1**) should be viewed with some caution, and it may not be correct to assign them structures typical of other α,β-unsaturated ketones.[5]

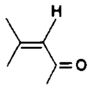
Additionally, there have been numerous reports of metal-catalyzed transformations and hydrogenations of mesityl oxide in which some kind of transient mesityl oxide complex may be likely to be involved as an intermediate.[6] Similarly, such intermediates are likely to be formed in condensation reactions of acetone promoted by transition-metal compounds.[3,4,7] The nature of such intermediates has not been established, and a simple coordination complex of **1** cannot automatically be assumed in view of the possible rearrangements than can occur, as already cited.

Indeed, so far as we can determine from a search of the literature, it seems that there is no prior example of the fully documented and unambiguous characterization of a simple complex in which mesityl oxide is demonstrably present in the molecular form **1**. Certainly, we can find no previous X-ray structure determination.

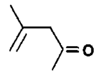
As part of our continuing studies[8-11] of organometallic compounds based upon CpRe and Cp*Re fragments (Cp = η-C_5H_5; Cp* = η-C_5Me_5), we have synthesized the rhenium mesityl oxide complex $Cp^*Re(CO)_2(Me_2C{=}CHCOCH_3)$ (**8**) and we now describe its full characterization by a combination of X-ray crystallography, ^1H and ^{13}C NMR, and IR spectroscopy. A related α,β-unsaturated ketone complex of a metal in the Mn, Tc, and Re group is $(CH_3C_5H_4)Mn(CO)_2(CH_2{=}CHCOMe)$.[12]



1a



1b



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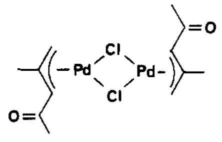

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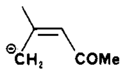

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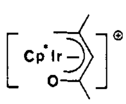

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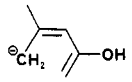

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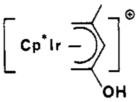

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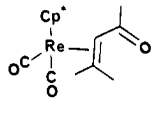
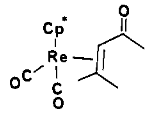
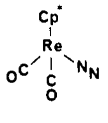


8a



8b



9

Experimental Section

Manipulations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled under nitrogen immediately before use. $Cp^*Re(CO)_2(N_2)$ was synthesized by irradiation of $Cp^*Re(CO)_3$ in THF followed by pressurization with N_2. This results in an approximate 3:2 mixture of $Cp^*Re(CO)_2(N_2)$ with $Cp^*Re(CO)_3$ which was used without further separation.[13] ^1H and ^{13}C NMR spectra were obtained by using a Bruker WM-400 instrument, IR spectra by using a Perkin-Elmer Model 983 instrument, and mass spectra by using a Hewlett-Packard Model 5985 mass spectrometer.

Preparation of (η-C_5Me_5)Re(CO)$_2$($Me_2C{=}CHCOMe$) (8). Method 1. $Cp^*Re(CO)_2(N_2)$ (150 mg of the mixture with $Cp^*Re(CO)_3$) was dissolved in acetone (15 mL) at room temperature, and then an excess (ca. 0.12 g) of solid $[Me_3O][BF_4]$ (Columbia Organic Chemical Co.) was added. The mixture was stirred for 24 h at 55 °C. After this time all the $Cp^*Re(CO)_2(N_2)$ complex had disappeared (by IR). Acetone was pumped off, and the brown oily residue was extracted twice with 15 mL of ether. The ether extract was chromatographed on a neutral alumina column (prepared in hexane). Using hexane as eluent first removed the $Cp^*Re(CO)_3$, and then THF–hexane (1:1) removed a slightly yellow band which contained the product. Recrystallization from hexane–diethyl ether gave 66 mg of colorless microcrystals of **8** (57% yield, with 50 mg of $Cp^*Re(CO)_3$ recovered), mp 138–140 °C. A similar yield was obtained by using $[Et_3O][BF_4]$ (CH_2Cl_2 solution; Columbia Organic Chemical Co.).

Method 2. $Cp^*Re(CO)_3$ (200 mg) was dissolved in 100 mL of freshly distilled THF and irradiated for 45 min at 0 °C under N_2. (This time is sufficient to provide a reasonable conversion to the THF complex $Cp^*Re(CO)_2(THF)$ without too much ensuing decomposition.) The volume was reduced to half under vacuum, and then about 1 mL of freshly distilled mesityl oxide (MCB Chemicals) was added, and the mixture stirred for 17 h at room temperature. The IR spectrum now showed that the THF com-

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[6] For recent examples see: (a) Hegedus, L. S.; Perry, R. J. *J. Org. Chem.* **1985**, *50*, 4955. (b) Smith, T. A.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *289*, 385. (c) Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1985**, *29*, 55. (d) Schaal, M.; Weigand, W.; Nagel, U.; Beck, W. *Chem. Ber.* **1985**, *118*, 2186. (e) Gibson, D. H.; El-Omrani, Y. S. *Organometallics* **1985**, *4*, 1473. (f) Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *J. Org. Chem.* **1982**, *47*, 4640. (g) Kogure, T.; Ojimi, I. *J. Organomet. Chem.* **1982**, *234*, 249.

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Table I. Summary of Crystal and X-ray Collection Data for $Cp^*Re(CO)_2(Me_2C{=}CHCOMe)$ (8)

compd	$Cp^*Re(CO)_2(Me_2C{=}CHCOMe)$
formula	$C_{18}H_{25}O_3Re$
space group	$P2_1/n$[a]
a, Å	8.515 (2)
b, Å	14.277 (4)
c, Å	15.093 (4)
β, deg	99.30 (2)
U, Å^3	1810.8
Z	4
d(calcd), g cm^{-3}	1.745
cryst dimens, mm	0.42 × 0.07 × 0.18
temp, °C	21
radiatn	Mo Kα
μ(Mo Kα), cm^{-1}	68.10
transmissn factors	0.239–0.662
scan type	ω–2θ
scan speed, deg min^{-1}	1.18–4.12
scan width, deg	$0.95 + 0.35 \tan\theta$
unique reflcns, ($0° < 2\theta < 48°$)	2846
obsd reflctns ($I \geq 3\sigma(I)$)	1885
no. of variables	199
R_F	0.034
R_{wF}	0.044
goodness of fit	1.140

[a] Alternative setting of $P2_1/c$; equivalent positions: x, y, z; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $-x, -y, -z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

Table II. Positional Parameters for $Cp^*Re(CO)_2(\eta^2\text{-}Me_2C{=}CHCOMe)$ (8)

atom	x	y	z	B_{eq},[a] Å^2
Re	0.18888 (5)	0.20158 (3)	0.25958 (3)	2.996 (19)
O(1)	0.2614 (16)	0.3168 (8)	0.1021 (8)	9.0 (9)
O(2)	0.3894 (13)	0.3363 (8)	0.3870 (8)	8.1 (7)
O(31)	0.5124 (12)	0.1322 (9)	0.1248 (7)	8.5 (10)
C(1)	0.2441 (16)	0.2702 (9)	0.1652 (10)	5.2 (7)
C(2)	0.3160 (15)	0.2842 (10)	0.3368 (9)	5.1 (8)
C(11)	−0.0730 (14)	0.2349 (11)	0.2187 (10)	5.4 (9)
C(12)	−0.0545 (14)	0.1383 (10)	0.2030 (7)	4.8 (9)
C(13)	−0.0101 (14)	0.0988 (10)	0.2880 (10)	5.3 (9)
C(14)	0.0024 (15)	0.1655 (13)	0.3507 (8)	5.9 (11)
C(15)	−0.0361 (15)	0.2515 (9)	0.3065 (10)	4.8 (8)
C(21)	−0.1403 (23)	0.3064 (21)	0.1512 (23)	18.8 (30)
C(22)	−0.1038 (19)	0.0943 (26)	0.1128 (14)	17.2 (35)
C(23)	0.0037 (24)	−0.0087 (15)	0.3028 (25)	18.7 (42)
C(24)	0.0350 (21)	0.1480 (25)	0.4503 (11)	16.3 (40)
C(25)	−0.0530 (24)	0.3396 (19)	0.3596 (23)	17.4 (32)
C(31)	0.2859 (19)	0.0522 (11)	0.0583 (10)	7.0 (9)
C(32)	0.3935 (15)	0.0965 (11)	0.1364 (9)	5.4 (7)
C(33)	0.3397 (11)	0.0837 (9)	0.2246 (7)	3.8 (6)
C(34)	0.4194 (13)	0.1195 (10)	0.3073 (10)	5.3 (8)
C(35)	0.4207 (20)	0.0644 (11)	0.3931 (11)	7.3 (9)
C(36)	0.5784 (16)	0.1722 (14)	0.3117 (11)	7.8 (13)

[a] $B_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table III. Selected Bond Lengths (Å) and Interbond Angles (deg) for $Cp^*Re(CO)_2(\eta^2\text{-}Me_2C{=}CHCOMe)$ (8)[a]

(a) Bond Lengths			
Re–C(1)	1.851 (14)	C(13)–C(14)	1.34 (2)
Re–C(2)	1.875 (13)	C(14)–C(15)	1.41 (2)
Re–C(aa)	2.266 (12)	C(15–C(11)	1.33 (2)
Re–C(12)	2.295 (12)	C(11)–C(21)	1.49 (2)
Re–C(13)	2.333 (12)	C(12)–C(22)	1.50 (2)
Re–C(14)	2.321 (11)	C(13)–C(23)	1.55 (2)
Re–C(15)	2.262 (11)	C(14)–C(24)	1.50 (2)
Re–$Cp^*_{centroid}$	1.974	C(15)–C(25)	1.51 (2)
Re–C(33)	2.232 (10)	C(31)–C(32)	1.51 (2)
Re–C(34)	2.330 (12)	C(32)–C(33)	1.49 (2)
C(1)–O(1)	1.19 (2)	C(32)–O(31)	1.17 (2)
C(2)–O(2)	1.17 (2)	C(33)–C(34)	1.42 (2)
C(11)–C(12)	1.41 (2)	C(34)–C(35)	1.51 (2)
C(12)–C(13)	1.40 (2)	C(34)–C(36)	1.54 (2)
Inter-Bond Angles			
C(1)–Re–C(2)	87.3 (6)	C(14)–C(13)–C(23)	127 (2)
C(1)–Re–C(33)	89.4 (5)	C(13)–C(14)–C(24)	125 (2)
C(1)–Re–C(34)	101.6 (5)	C(15)–C(14)–C(24)	128 (2)
C(2)–Re–C(33)	109.0 (5)	C(11)–C(15)–C(25)	130 (2)
C(2)–Re–C(34)	75.4 (6)	C(14)–C(15)–C(25)	121 (2)
C(33)–Re–C(34)	36.4 (5)	C(31)–C(32)–C(33)	114 (1)
Re–C(1)–O(1)	172 (1)	C(31)–C(32)–O(31)	120 (1)
Re–C(2)–O(2)	177 (1)	C(33)–C(32)–O(31)	126 (1)
C(12)–C(11)–C(1)	109 (1)	Re–C(33)–C(32)	113 (1)
C(11)–C(12)–C(13)	105 (1)	Re–C(33)–C(34)	74 (1)
C(12)–C(13)–C(14)	110 (1)	C(32)–C(33)–C(34)	125 (1)
C(13)–C(14)–C(15)	107 (1)	Re–C(34)–C(33)	69 (1)
C(14)–C(15)–C(11)	108 (1)	Re–C(34)–C(35)	115 (1)
C(12)–C(11)–C(21)	127 (2)	Re–C(34)–C(36)	118 (1)
C(15)–C(11)–C(21)	124 (2)	C(33)–C(34)–C(35)	120 (1)
C(11)–C(12)–C(22)	123 (2)	C(33)–C(34)–C(36)	120 (1)
C(13)–C(12)–C(22)	131 (2)	C(35)–C(34)–C(36)	109 (1)
C(12)–C(13)–C(23)	122 (2)		

[a] Esd's in the last digits given in parentheses.

plex had almost totally reacted and absorptions at 1956 and 1887 cm^{-1} indicated the formation of the mesityl oxide complex 8. Purification was carried out as described in method 1. The yield after recrystallization was 65 mg (27.6% based on $Cp^*Re(CO)_3$).

Anal. Calcd for $C_{18}H_{25}O_3Re$: C, 45.47; H, 5.26. Found: C, 45.90; H, 5.51. IR (KBr, cm^{-1}): 1953 (vs), 1881 (vs) (ν(CO)), 1670 (s) (ketonic C=O). IR (hexane, cm^{-1}): 1966, 1958, 1902, 1883 all (vs) (ν(CO)), 1690 (w) and 1655 (w) (ketonic C=O). IR (CH_2Cl_2, cm^{-1}): 1955 (vs) and 1881 (vs) (ν(CO)), 1669 (m) (ketonic C=O). ^{1}H NMR ($CDCl_3$): δ 1.67 (s, 3 H, CH_3), 1.99 (s, 15 H, C_5Me_5), 2.14 (s, 3 H, Me), 2.21 (s, 3 H, Me), 2.68 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$): δ 10.48 (q, $^1J_{CH}$ = 128.0 Hz, C_5Me_5), 28.38 (q, $^1J_{CH}$ = 127.7 Hz, Me), 30.40 (q, $^1J_{CH}$ = 126.5 Hz, Me), 32.56 (q, $^1J_{CH}$ = 126.8 Hz, Me), 51.05 (d, $^1J_{CH}$ = 144.4 Hz, CH), 58.39 (s, CMe_2), 98.58 (s, C_5Me_5), 202.73 (s), 205.90 (s) and 207.30 (s, CO's). MS (EI, ^{187}Re): m/z 476 (M^+), 448 ($M^+ - CO$).

X-ray Structure Determination for $Cp^*Re(CO)_2(Me_2C{=}CHCOMe)$ (8). Data were collected on an Enraf-Nonius CAD4-F diffractometer equipped with a graphite monochromator and were corrected for Lorentz, polarization, and absorption effects.[14a] A total of 2846 reflections were collected, of which 1885 were considered to be observed ($I \geq 3\sigma(I)$) and used in subsequent calculations. Pertinent crystal and experimental parameters are given in Table I.

The structure was solved by conventional heavy-atom methods and refined by full-matrix least squares. The positions of some methyl group hydrogen atoms were located in difference Fourier syntheses and were used to determine calculated positions for the remaining hydrogen atoms of the methyl groups, with d(C–H) = 0.95 Å. The olefinic proton (H(331)) was fixed in the position determined in a Fourier synthesis. All non-hydrogen atoms were refined anisotropically, and the isotropic temperature factors of the hydrogen atoms were set at (U_{eq} + 0.01) Å^2 where U_{eq} are the values of the equivalent isotropic temperatures of the atoms to which they are bonded. The refinement was considered complete when the ratio of all calculated shifts to esd's was less than 0.1.

The final residuals were $R = 0.034$ and $R_w = 0.044$, and the goodness of fit was 1.140. During the final cycles of refinement the weighting scheme employed was $w = [\sigma(F_o) + 0.0009F_o^2]^{-1}$. There were no significant trends in $\langle w(|F_o| - |F_c|)^2\rangle - |F_c|)^2$ with either F_o or $(\sin\theta)/\lambda$. The largest peak in a final difference map was of height 0.96 (15) e Å^{-3} and was situated 0.96 Å from the Re atom. Complex neutral atomic scattering factors were taken from ref 14b. Computer programs[15] were run on an in-house VAX 11-750. Positional parameters are given in Table II. Selected bond distances and interbond angles are listed in Table III. Anisotropic thermal parameters (Table V), calculated hydrogen

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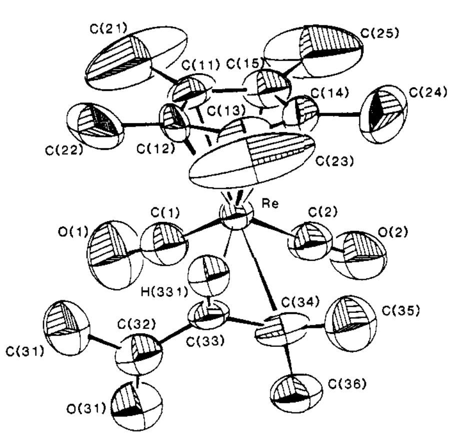

Figure 1. A perspective view of a molecule of Cp*Re(CO)$_2$(η^2-$Me_2C{=}CHCOMe$) (8) with atom numbering.

atom coordinates (Table VI), and tables of calculated and observed structure factors are available as supplementary material.

Results and Discussion

(a) Synthesis. We first observed the mesityl oxide complex 8 to be formed during reactions of the dinitrogen complex Cp*Re(CO)$_2$(N_2) (**9**) with the electrophiles [Me_3O][BF_4] or [Et_3O][BF_4] conducted in acetone. We were, in fact, seeking an alkylation route for the conversion of the coordinated dinitrogen to an alkyldiazenide ligand, to thereby synthesize the unknown complexes [Cp*Re(CO)$_2$(N_2R)]$^+$ (R = Me, Et), being counterparts of the well-known aryldiazenide analogues.[10] Characterization of the colorless, air-stable crystalline product obtained in 57% yield after chromatography as a mesityl oxide complex was subsequently supported by its synthesis directly from the labile THF solvate Cp*Re(CO)$_2$(THF) (generated "in situ" by irradiation of Cp*Re(CO)$_3$ in THF) and mesityl oxide. Complex 8 is stable indefinitely as a solid, and no deterioration has been observed in organic solvents under nitrogen for periods of at least a day. Solutions in hexane pressurized to 2000 psi with N_2 for 24 h at room temperature or in contact with 1 atm of CO for 24 h showed no displacement of the mesityl oxide ligand by N_2 or CO. However, reaction with I_2 in diethyl ether occurred stereospecifically to produce *cis*-Cp*Re(CO)$_2$$I_2$[13] as the only organometallic product.

At the present time, we do not know the route by which the dinitrogen complex is converted into 8. However, some relevant details may be noted. (i) Cp*Re(CO)$_2$(N_2) is inert to dissociation of the N_2 molecule at room temperature since we find that there is no exchange of the ^{15}N-labeled ligand with $^{14}N_2$ over 5 days at room temperature in hexane at pressures up to 2000 psi. (ii) Complex 8 is not formed when Cp*Re(CO)$_2$(N_2) is treated with mesityl oxide. Therefore, we do not consider it likely that mesityl oxide is simply being produced in a well-known[16] electrophilically catalyzed aldol concentration of acetone and subsequently coordinating to rhenium by displacement of N_2. (iii) No formation of 8 was observed when Cp*Re(CO)$_2$(N_2) was heated in acetone for 24 h at 55 °C, so it does not appear to involve an aldol condensation induced by the rhenium complex alone.[17]

(b) X-ray Structure. The solid-state structure of 8, as determined by X-ray crystallography, is illustrated in Figure 1. The structure consists of discrete monomeric molecules of Cp*Re(CO)$_2$(η^2-$Me_2C{=}CHCOMe$) with the ligand unambiguously present as a mesityl oxide molecule (1) coordinated to rhenium by the olefinic group only and adopting the s-cis conformation (**1a**). The structural results clearly rule out any possibility that the ligand might be present as the isomer **2** or as either of the deprotonated forms 4 or 6. All three C–C(methyl) bond lengths are near 1.52 Å as expected, the rhenium is bound to the carbon atoms in the 3- and 4-positions C(33) and C(34) only, and the C(32)—O(31) length is that of a typical ketonic C=O group (1.17 (2) Å).

Table IV. Torsion Angles γ and δ (deg) for Olefin Coordination in Compound 8[a]

Defining atoms	torsion angle
(a) angle γ	
C(32)C(33)C(34)C(35)	145 (2)
(b) angle δ	
ReC(32)C(33)C(34)	108 (1)
ReC(33)C(34)C(35)	107 (1)
ReC(33)C(34)C(36)	111 (1)

[a] Angles γ and δ are defined in ref 19.

Coordination of the olefin to the metal has produced the geometrical changes expected from the Dewar–Chatt–Duncanson model[18] of synergic donation of electron density from the olefinic π orbital, together with back-donation from filled metal d orbitals to the olefinic π^* orbital. This results in a lengthening of the C–C double bond to 1.42 (2) Å and a bending back of the substituents on the olefin away from the metal. The degree of deformation observed can be seen in the torsion angles about the double bond. The values of these angles γ and δ as defined by Ittel and Ibers[19] are given in Table IV and are typical for olefin complexes. The orientation of the axis of the C(33)–C(34) olefinic bond is more or less parallel to the plane of the cyclopentadienyl ring, rather like the situation in a previously studied[8] alkyne complex, CpRe(CO)$_2$(C_2Ph_2). Depending whether the olefin is considered to occupy one or two coordination sites, the complex may be described to have a three- or four-legged "piano-stool" geometry.

There are a number of regular, sensible chemical features in the apparent distribution of bond lengths in this molecule, although as is frequently the case, the validity is limited somewhat by the precision in the atom positions. The Re–C(33) bond to the olefin at 2.232 (10) Å is significantly shorter than the Re–C(34) bond (2.330 (12) Å) (see below); at the same time it is "opposite" what may be the longer of the two Re–C(carbonyl) bonds Re–C(2) (1.875 (13) Å) rather than Re–C(1) (1.851 (14) Å). Considering the Re–C distances to the Cp* group, these are not equal (χ^2 = 30.45) and follow a pattern with the longer distances Re–C(12) = 2.295 (12) Å, Re–C(13) = 2.333 (12) Å, and Re–C(14) = 2.321 (11) Å all involving carbon atoms "opposite" carbonyl groups, while the shorter distances Re–C(11) = 2.266 (12) Å and Re–C(15) = 2.262 (11) Å are "opposite" the olefin. Such a pattern has been observed previously,[13] and we think it reflects the better ability of the CO ligand rather than the olefin to withdraw π-electron density. The Re–Cp*(centroid) distance of 1.974 Å seems to be rather longer than in some related structures we have determined.[8,13]

Since mesityl oxide is an unsymmetrical olefin, the differing Re–C(olefin) bond lengths are not surprising. The shorter bond is observed to be to the carbon atom C(33) bearing the keto function. The factors responsible for this are unclear. Model calculations on complexes of unsymmetrical olefins containing π-donor or π-acceptor groups[20]

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(which cause a polarization of the olefin π and π* orbitals[21]) suggest in most cases that the stronger bond is to the olefinic carbon that does not carry the π-donor or π-acceptor group.

(c) Spectroscopic Properties. The IR spectrum of complex 8 in a KBr disk or in CH_2Cl_2 solution shows two very strong but quite broad ν(ReCO) absorptions in the 1880–1960 cm^{-1} region. Furthermore, a third strong absorption at 1670 cm^{-1} for the keto group is also observed. However, in nonpolar solvents like hexane or cyclohexane, the IR spectrum shows four strong sharp absorptions at 1966, 1958, 1902, and 1883 cm^{-1} assignable as ν(ReCO) as well as two weak ketonic ν(CO) at 1690 and 1655 cm^{-1}. The better resolution obtainable in nonpolar solvents thus allows the identification of two species in solution, which we consider most likely to be the complexes **8a** and **8b**, containing mesityl oxide in the s-cis and s-trans conformations respectively, present in an equilibrium mixture. A similar interpretation has been given for the appearance of two sets of ν(CO) absorptions in the solution spectra of a variety of π-hetero-1,3-diene complexes of iron,[22–24] and the effect has also been noted with selected ruthenium examples.[25]

Mesityl oxide has been shown by a variety of methods[26,27] to be predominantly in the s-cis conformation. Although there has been some ambiguity in assigning the ^1H NMR spectrum,[28] the correct assignment for the spectrum in CCl_4 now seems generally agreed[27,28] to be δ 1.85 (d, 1.4 Hz, Me trans to COMe), 2.11 (d, 1.2 Hz, Me cis to COMe), 2.19 (s, COMe), and 5.97 (s, H). We observed essentially the same spectrum for mesityl oxide in $CDCl_3$ solution. The ^1H NMR spectrum of 8 exhibits a single set of resonances and is unchanged over the temperature range +50 °C ($CDCl_3$) to −80 °C (CS_2). The ^{13}C NMR spectrum also shows a single set of resonances at room temperature. These results we attribute to an averaging of the resonances for the isomers **8a** and **8b** in rapid equilibrium. Since there is no observed formation of $Cp^*Re(CO)_3$ when a solution of 8 is in contact with 1 atm of CO for 24 h, it seems reasonable to assume that there is negligible dissociation of mesityl oxide from the complex in solution at room temperature. In agreement with this, the ^1H NMR of a mixture of 8 and mesityl oxide is merely a superposition of the individual resonances. A substantial upfield coordination shift of the olefinic proton is observed for 8, and there are significant changes in the methyl resonances. An unambiguous assignment of the latter is hindered by the fact that all three methyls now appear as singlets; i.e., the small couplings of the allylic methyls to the proton, observable in the pure ligand, are absent. The olefinic proton coordination shift (from δ 5.88 in mesityl oxide to δ 2.68 in 8) is typical of the large shifts experienced by "outer" protons in coordinated dienes.[29]

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Registry No. 8, 104780-28-1; $Cp^*Re(CO)_2(N_2)$, 92787-15-0; $Cp^*Re(CO)_3$, 12130-88-0; $Cp^*Re(CO)_2(THF)$, 90695-84-4; acetone, 67-64-1; mesityl oxide, 141-79-7.

Supplementary Material Available: Anisotropic thermal parameters (Table V) and calculated hydrogen atom coordinates for compound 8 (Table VI) (2 pages); a listing of observed and calculated structure factors for compound 8 (Table VII) (20 pages). Ordering information is given on any current masthead page.

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