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Characterization of the Two-Electron η^2-Alkyne Ligand in Cyclopentadienyldicarbonyl(alkyne)rhenium Complexes. X-ray Structure of $Re(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2Ph_2)(CO)_2$

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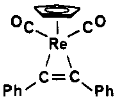
The complexes $CpRe(CO)_2(C_2Ph_2)$ (**1a**) and $CpRe(CO)_2(PhC_2Me)$ (**1b**) have been synthesized directly in moderate yield from $CpRe(CO)_2(THF)$ and the alkyne in hexanes and have been fully characterized, including an X-ray structure for **1a**. Complex **1a** crystallizes in space group $P2_1/n$ of the monoclinic system with a = 10.841 (1) Å, b = 13.961 (2) Å, c = 23.121 (2) Å, β = 91.360 (8)°, and Z = 8. The observed and calculated densities are 1.53 (1) and 1.490 g cm^{-3}, respectively. Using 3008 unique data in the range $2.5° < 2\theta < 45°$ (Mo Kα) with $I > 3.0\sigma(I)$, the structure was solved and refined by full-matrix least-squares methods to $R_F = 0.0295$ and $R_{wF} = 0.0340$. The asymmetric unit contains two crystallographically independent, discrete mononuclear molecules (1 and 2) of $CpRe(CO)_2(C_2Ph_2)$ which differ principally by a minor variation in the relative orientation of the phenyl rings of the C_2Ph_2 ligand. Bond length and angle differences in the two molecules are insignificant. The C_2Ph_2 ligand is η^2-bonded to rhenium and functions as a two-electron donor; it is bent into a cis geometry, but the cis deformation angles (149.9 (9)°–152.6 (10)°) are among the largest, and the C≡C bond lengths (1.261 (14) Å in molecule 1 and 1.232 (13) Å in molecule 2) are among the shortest that have been observed for coordinated diphenylacetylene. Nevertheless, **1a** is remarkably robust, undergoing no reaction with CO (1200 psi) or with PPh_3 at ambient temperature. The η^2-C_2Ph_2 ligand is symmetrically placed with respect to the two carbonyl groups in 1 and 2, such that each molecule approximates a "four-legged piano stool" geometry, and it is coordinated symmetrically to rhenium, with bond lengths of 2.188 (10) Å and 2.182 (9) Å in molecule 1 and 2.190 (9) Å and 2.194 (9) Å in molecule 2. The variable-temperature ^{13}C NMR spectra of **1b** indicate restricted rotation of the alkyne ligand about the rhenium–alkyne axis and show that this ligand is oriented parallel to the Cp ring in the frozen-out structure, consistent with the crystal structure of **1a**.

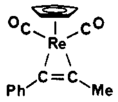
Introduction

There is current interest in the preparation of heterometallic acetylene cluster compounds and much of their chemistry has been reviewed recently.[1] Systematic procedures for the synthesis of heterotrimetallic examples are being developed, and among these is the thermal addition of a unit comprising the third metal to a preformed heterobimetallic acetylene framework. In this way, we[2] and others[3] have synthesized heterotrimetallic clusters of the type $CpNiCoFe(CO)_6(C_2RR')$ (Cp = η^5-C_5H_5; R, R′ = alkyl or phenyl (Ph)), for example by reacting $Fe_2(CO)_9$ with $CpNiCo(CO)_3(C_2RR')$. The method can be extended to give the clusters $CpNiCoM(CO)_6(C_2RR')$ (where M = Ru or Os) by employing $Ru(CO)_5$ or $Os(CO)_5$ instead, and the structures of these will be reported elsewhere.[4]

We were interested in exploring the possible further generality of this method in the synthesis of the corresponding unknown manganese group analogues incorporating the CpM(CO) fragment (where M = Mn or Re), e.g., $Cp_2NiCoRe(CO)_4(C_2RR')$. In such an attempt, using $CpRe(CO)_2(THF)$ (THF = tetrahydrofuran) and $CpNiCo(CO)_3(C_2Ph_2)$,[5] no trimetallic cluster was obtained but the mononuclear rhenium alkyne complex $CpRe(CO)_2(C_2Ph_2)$ was isolated in low yield. This compound had been synthesized in 1976 by Nesmeyanov et al., and some properties were very briefly reported at the time.[6] We know of no further studies on it. Consequently, we have synthesized the compound directly from $CpRe(CO)_2(THF)$ and Ph_2C_2 and have carried out a complete characterization, including an X-ray structure determination. The analogous complex $CpRe(CO)_2(PhC_2Me)$ has also been synthesized and subjected to variable-temperature NMR so as to study the dynamic behavior of the η^2-alkyne ligand.



1a



1b

Results and Discussion

Synthesis. $CpRe(CO)_2(C_2Ph_2)$ (**1a**) was initially observed to be formed in low yield as yellow crystals in the reaction of $CpNiCo(CO)_3(C_2Ph_2)$ with $CpRe(CO)_2(THF)$. Other than this, only unidentified decomposition products and $CpRe(CO)_3$ were observed. The majority of the $CpNiCo(CO)_3(C_2Ph_2)$ was recovered. In 1976, Nesmeyanov et al. reported the synthesis of **1a** in 20% yield by stirring a solution of $CpRe(CO)_2(THF)$ (formed in situ in THF by irradiation of $CpRe(CO)_3$ at 10 °C for 30 min) and Ph_2C_2 for a further 15 min at 20 °C with no further irradiation.[6] In our hands, this procedure was ineffective at 20 °C and, furthermore, it gave **1a** in only ca. 5% yield at 45 °C, along with extensive decomposition. The yield improved to ca. 15% when the reaction of excess Ph_2C_2 with a concentrated THF solution of $CpRe(CO)_2(THF)$ was conducted in hexanes at 20 °C. Finally, **1a** was obtained in ca. 30% yield by reacting a large excess of Ph_2C_2 with crystalline $CpRe(CO)_2(THF)$ entirely in hexanes at 20 °C. The analogous complex $CpRe(CO)_2(PhC_2Me)$ (**1b**) was similarly synthesized. The in situ irradiation of excess Ph_2C_2 and $CpRe(CO)_3$ in hexanes produced **1a** in rather low yield.

Properties. $CpRe(CO)_2(C_2Ph_2)$ (**1a**) is a pale yellow crystalline solid which is soluble in hexane and polar organic solvents. It melts at 129–132 °C and its solutions

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Table I. Selected Interatomic Distances (Å) and Angles (deg) for $CpRe(CO)_2(C_2Ph_2)$ (1a)

Metal Atom Coordination					
Bond Lengths					
Re(1)-C(11)	1.893 (11)	Re(1)-Cp(center)	2.039 (12)	Re(2)-C(23)	2.190 (10)
Re(1)-C(12)	1.906 (12)	Re(2)-C(21)	1.916 (11)	Re(2)-C(24)	2.194 (10)
Re(1)-C(13)	2.188 (10)	Re(2)-C(22)	1.901 (10)	Re(2)-Cp(center)	1.968 (12)
Re(1)-C(14)	2.182 (10)				
Bond Angles					
C(13)-Re(1)-C(14)	33.5 (4)	Re(1)-C(11)-O(11)	177.2 (9)	Re(2)-C(23)-C(211)	134.5 (7)
Re(1)-C(13)-C(14)	73.0 (6)	Re(1)-C(12)-O(12)	177.6 (10)	Re(2)-C(24)-C(25)	136.4 (7)
Re(1)-C(14)-C(13)	73.5 (6)	C(23)-Re(2)-C(24)	32.7 (3)	Re(2)-C(21)-O(21)	177.2 (9)
Re(1)-C(13)-C(111)	134.4 (7)	Re(2)-C(23)-C(24)	73.8 (6)	Re(2)-C(22)-O(22)	178.4 (9)
Re(1)-C(14)-C(15)	135.3 (7)	Re(2)-C(24)-C(23)	73.5 (6)		
Acetylene Coordination					
Bond Lengths					
C(13)-C(14)	1.261 (14)	C(14)-C(15)	1.43 (1)	C(23)-C(211)	1.44 (1)
C(13)-C(111)	1.45 (1)	C(23)-C(24)	1.232 (13)	C(24)-C(25)	1.46 (1)
Bond Angles					
C(14)-C(13)-C(111)	152.6 (10)	C(24)-C(23)-C(211)	151.6 (9)	C(23)-C(24)-C(25)	149.9 (9)
C(13)-C(14)-C(15)	151.1 (10)				

show remarkable thermal stability. It was recovered unchanged after 8 h in refluxing isooctane (99 °C). The solid and its hexane solution are also stable in air for periods exceeding 1 week and 12 h, respectively. The PhC_2Me complex **1b** was obtained as a pale yellow, low-melting solid which appeared to be much less stable and exhibited decomposition within a few hours when exposed to air.

Both compounds display the expected two ν(CO) absorptions in the infrared spectrum near 1980 and 1900 cm^{-1}, and their mass spectra indicate them to be monomeric in the vapor phase. Their major fragmentation is the expected sequential loss of the CO groups. The ^1H NMR spectra of **1a** and **1b** are unexceptional; the Cp resonances occurring near δ 5.5, the phenyl multiplet at δ 7.3–7.9, and the methyl in **1b** at δ 2.75. The ^{13}C NMR spectrum of **1a** in $CDCl_3$ is also as expected with the acetylenic carbon resonance of δ 81.7 and CO at δ 204.5. That of **1b**, containing the unsymmetrical alkyne PhC_2Me, exhibits, at ambient temperature, a single carbonyl carbon resonance at δ 204.9 (indicating dynamic behavior of the alkyne ligand) and the PhC and MeC acetylenic carbon resonance at δ 69.4 and 78.2, respectively.

In attempts to substitute either the Ph_2C_2 ligand or a carbonyl group in **1a**, we have found the complex to be remarkably inert and robust. No reaction occurred with triphenylphosphine in either hexanes, octane, or acetonitrile at or somewhat above room temperature, and, in the case of acetonitrile, no substitution by the solvent occurred. Similarly, no reaction was observed with **1a** in hexanes and CO at either 1 atm or 1200 psi of pressure and no decomposition of **1a** occurred. This is notably in contrast with, for example, the behavior of $Cp_2Ti(CO)(C_2Ph_2)$[7] in which the diphenylacetylene group is readily substituted by CO to give $Cp_2Ti(CO)_2$ and decomposition of $Cp_2Ti(CO)(C_2Ph_2)$ is rapid above ca. 30 °C. Refluxing **1a** in THF produced rapid decomposition.

X-ray Structure of $CpRe(CO)_2(C_2Ph_2)$ (1a). The structure is composed of discrete, mononuclear molecules. The asymmetric unit contains two independent molecules, referred to as molecules 1 and 2. Molecule 1 is illustrated in Figure 1, which also provides the numbering scheme. The differences between these crystallographically distinct molecules are only minor and are discussed below. Relevant interatomic distances and interbond angles are listed in Table I. The geometry of the rhenium coordination sphere conforms to that of a four-legged "piano stool", with the Cp ring as the seat and the four carbons (e.g., C(11) and C(12) from the CO groups and the acetylenic carbons C(13) and C(14) of the Ph_2C_2 ligand in molecule 1) as the base. The plane of these four carbons is virtually parallel to the Cp plane; the observed dihedral angle between these planes being 2.3 (5)° and 1.9 (5)° in molecules 1 and 2, respectively. The small "bite" of the η^2-diphenylacetylene ligand precludes any expectation of approximate fourfold symmetry for these basal carbon atoms, but the Ph_2C_2 ligand is quite symmetrically located in each independent molecule. The rhenium is equidistant from the two acetylenic carbon atoms at an average distance of Re–C = 2.189 (10) Å.

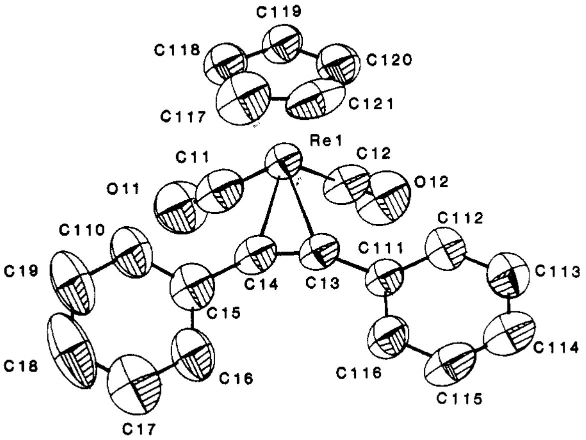

Figure 1. A view of molecule 1 in $CpRe(CO)_2(C_2Ph_2)$ showing the square-based piano-stool configuration and the atom numbering scheme.

The coordinated diphenylacetylene is bent into a cis geometry with observed Ph—C≡C deformation angles ranging from 149.9 (9) to 152.6 (10)°. This bending of a coordinated alkyne ligand has been observed in all previous mononuclear structures, but it is noteworthy that the cis deformation angles observed here are among the largest that have been found, the reported range[7-20] being

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Table II. The C≡C Bond Lengths (Å), Cis Deformation Angles (deg), and ν(C≡C) Values (cm^{-1}) in Some Mononuclear η^2-Diphenylacetylene Complexes

complex	d(C≡C)	Ph—C≡C angle	ν(C≡C)	ref
PhC≡CPh	1.198 (3)	178.1 (2)	2223	21, 22
$CpRe(CO)_2(C_2Ph_2)$	1.261 (14)	152.6 (10), 151.1 (10)	1848	a
	1.232 (13)	151.6 (9), 149.9 (9)		
$[Co(C_2Ph_2)(PMe_3)_3]^+$	1.265 (7)	143.6 (5), 137.5 (5)		16
$[Co(MeCN)(C_2Ph_2)(PMe_3)_3]^+$	1.267 (7)	147.0 (5), 148.8 (5)	1780	16
$Cp_2Mo(C_2Ph_2)$	1.269 (7)			15
$CpNb(CO)(C_4Ph_4)(C_2Ph_2)$	1.26 (4)	142 (3)	1780	10
$Pt(C_2Ph_2)_2$	1.291 (5)	152.4 (5), 154.1 (5)	1881	8
$Ni(C_2Ph_2)(CNBu\text{-}t)_2$ ^{b}	1.276 (12)	148.2 (10), 147.5 (11)	1810	9
	1.291 (16)	147.2 (14), 151.3 (14)		
$Cp_2Ti(CO)(C_2Ph_2)$	1.285 (10)	138.8 (7), 145.8 (7)	1780	7
$[CpMo(CO)(PPh_3)(C_2Ph_2)]^+$	1.29 (2)	135 (1), 141 (1)	1645	19
$CpW(O)Ph(C_2Ph_2)$	1.29 (3)	143.5 (4)	1748	11
$Cp_2Nb(O_2CBu\text{-}t)(C_2Ph_2)$	1.29 (1)	141.2 (7), 146.4 (8)	1800	20
$W(CO)(C_2Ph_2)_3$	1.30	140	1702	12
$Pt(C_2Ph_2)(PPh_3)_2$	1.32 (9)	140	1740, 1768	13
$[pyH][TaCl_4(py)(C_2Ph_2)]$	1.325 (12)	138.2 (8), 141.2 (8)		17
$Mo(TTP)(C_2Ph_2)C_6H_5CH_3$	1.324 (5)	136.4 (4), 145.4 (4)		15
$Cp^*TaCl_2(C_2Ph_2)$	1.337 (8)	138.5 (5), 140.3 (5)		18
$CpNb(C_2Ph_2)_2(CO)$	1.35 (2)	138 (4)		14

^{a} This work. Values are for independent molecules 1 and 2, respectively. ^{b} Two independent molecules occur in the asymmetric unit.

Table III. Selected Dihedral Angles (deg) in $CpRe(CO)_2(C_2Ph_2)$

	atoms defining plane			
plane	molecule 1		molecule 2	
phenyl	C(111)-C(113)-C(115)	16.2	C(211)-C(213)-C(215)	28.2
phenyl	C(15)-C(17)-C(19)		C(25)-C(27)-C(29)	
C≡C—C(phenyl)	C(13)-C(14)-C(111)	16.1 (δ)	C(23)-C(24)-C(211)	18.3 (δ)
phenyl	C(111)-C(113)-C(115)		C(211)-C(213)-C(215)	
C≡C—C(phenyl)	C(13)-C(14)-C(15)	2.2 (δ)	C(23)-C(24)-C(25)	2.7 (δ)
phenyl	C(15)-C(17)-C(19)		C(25)-C(27)-C(29)	
C≡C—C(phenyl)	C(13)-C(14)-C(15)	2.6 (γ)	C(23)-C(24)-C(25)	7.8 (γ)
C≡C—C(phenyl)	C(13)-C(14)-C(111)		C(23)-C(24)-C(211)	

135–154° (Table II). In agreement with these somewhat large observed deformation angles, the observed C≡C bond lengths of 1.261 (14) and 1.232 (14) Å (which do not differ significantly in the two independent molecules) are short compared with other reported values in Table II, which range from 1.26 to 1.35 Å. Dimensionally, the ligand in the rhenium complex is therefore believed to be one of the least perturbed upon coordination, compared to the free diphenylacetylene (which has d(C≡C) = 1.198 (3) Å; Ph—C≡C = 178.1 (2)°).[21,22] In view of this, the reluctance

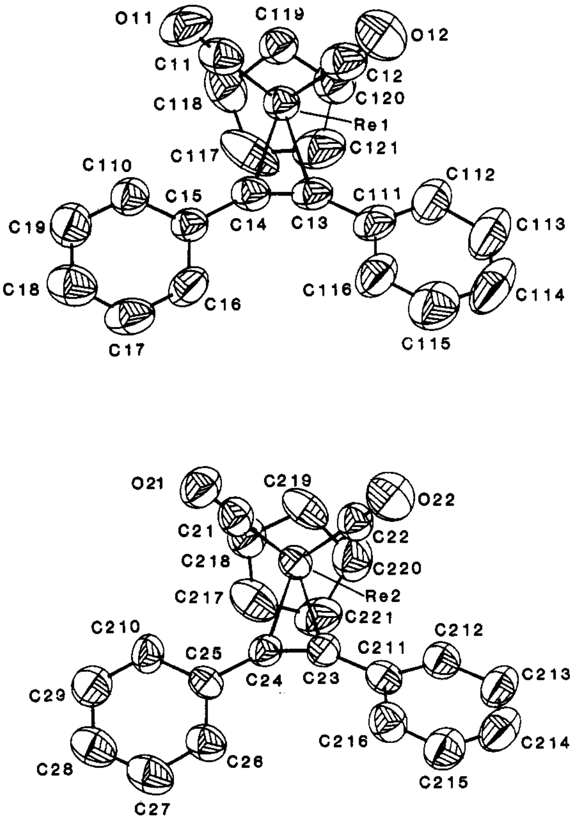

Figure 2. Projection of molecules 1 and 2 in $CpRe(CO)_2(C_2Ph_2)$ on the planes of the Cp rings, showing the minor variation in the relative orientation of the Cp rings and the phenyl rings of the C_2Ph_2 ligands.

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Table IV. Summary of Crystal Data and Intensity Collection for $CpRe(CO)_2(C_2Ph_2)$

compd	$C_{21}H_{15}O_2Re$
mol wt	485.55
a, Å	10.841 (1)
b, Å	13.961 (2)
c, Å	23.121 (2)
β, deg	91.360 (8)
cell vol, Å^3	3498
Z	8
ρ(calcd) g cm^{-3}	1.490
ρ(obsd) g cm^{-3}	1.53 (1)
space group	$P2_1/n$
cryst dimens, mm	0.06 × 0.11 × 0.30
t, °C	21
radiatn	Mo K*α* (graphite monochromated)
linear abs coeff, cm^{-1}	70.5
transmissn factors	0.447-0.993 (empirical)
scan speed, deg/min	0.8-4.0 (*θ*-2*θ* scan)
2*θ* limits, deg	2.5, 45.0
check reflctns	402 and 008 every 150 reflections
data collected	+*h*, +*k*, ±*l*, 4545
unique data, $I > 3.0\sigma(I)$	3008
R_F, %	2.95
R_{wF}, %	3.40
goodness of fit	1.17

of this ligand to undergo replacement by CO or PPh_3 is quite remarkable. The cis deformation of the acetylene ligand occurs more or less coplanar with the rhenium–acetylene metallacycle, as indicated by the very small dihedral angles (ca. 3°) between the plane of this metallacycle and the (phenyl)C—C≡C—C(phenyl) skeletal plane in each molecule.

The most obvious dissimilarity between the independent molecules 1 and 2, which are compared in Figure 2 projected onto the plane of the Cp ring, is in the relative orientation of the two phenyl rings in each case, most evident by comparing the dihedral angles between the planes of these phenyl rings.[23] In molecule 1, this angle is 16.2 (9)° and in molecule 2 it is 28.2 (9)°. In the determination of the X-ray structure of $Ni(C_2Ph_2)(CNBu\text{-}t)_2$, which also crystallizes with two independent molecules in the asymmetric unit, Dickson and Ibers[9] observed an analogous difference in these dihedral angles to be the main dissimilarity to the molecules. They noted that two contributing features may be calculated: (i) *δ*, the dihedral angle between an individual phenyl ring plane and its adjacent C≡C—C(phenyl) skeletal plane, and (ii) *γ*, a "tilt" angle which is the angle between the two distinguishable adjacent C≡C—C(phenyl) skeletal planes in the diphenylacetylene ligand. These values for 1a are listed in Table III.

Table V. Positional Parameters for $CpRe(CO)_2(C_2Ph_2)$

atom	*x*	*y*	*z*
	Molecule 1		
Re(1)	0.07979 (4)	0.16622 (3)	0.09831 (2)
C(11)	0.1422 (9)	0.0563 (7)	0.0610 (5)
C(12)	0.0553 (10)	0.0788 (8)	0.1603 (5)
O(11)	0.1774 (8)	−0.0137 (6)	0.0395 (4)
O(12)	0.0370 (8)	0.0255 (6)	0.1965 (4)
C(13)	0.2242 (9)	0.2255 (7)	0.1555 (5)
C(14)	0.2693 (8)	0.2183 (7)	0.1059 (4)
C(15)	0.3679 (8)	0.2329 (7)	0.0660 (4)
C(16)	0.4779 (10)	0.2744 (8)	0.0863 (5)
C(17)	0.5750 (9)	0.2861 (8)	0.0495 (6)
C(18)	0.5658 (10)	0.2562 (8)	−0.0069 (6)
C(19)	0.4602 (10)	0.2156 (9)	−0.0280 (5)
C(110)	0.3638 (10)	0.2053 (7)	0.0092 (4)
C(111)	0.2309 (10)	0.2519 (7)	0.2163 (5)
C(112)	0.1275 (12)	0.2616 (9)	0.2487 (5)
C(113)	0.1369 (15)	0.2938 (9)	0.3050 (5)
C(114)	0.2509 (14)	0.3126 (9)	0.3315 (6)
C(115)	0.3541 (14)	0.3003 (9)	0.2977 (6)
C(116)	0.3460 (12)	0.2708 (8)	0.2417 (5)
C(117)	0.0379 (10)	0.3047 (9)	0.0482 (6)
C(118)	−0.0177 (10)	0.2293 (9)	0.0183 (5)
C(119)	−0.1063 (9)	0.1897 (7)	0.0533 (5)
C(120)	−0.1075 (10)	0.2397 (8)	0.1042 (5)
C(121)	−0.0206 (12)	0.3105 (8)	0.1030 (6)
	Molecule 2		
Re(2)	0.27088 (4)	0.87942 (3)	0.66720 (2)
C(21)	0.3365 (9)	0.7683 (7)	0.6302 (4)
C(22)	0.2314 (9)	0.7893 (8)	0.7256 (4)
O(21)	0.3708 (7)	0.7013 (5)	0.6075 (3)
O(22)	0.2087 (8)	0.7331 (6)	0.7601 (4)
C(23)	0.4086 (8)	0.9317 (7)	0.7305 (4)
C(24)	0.4616 (8)	0.9261 (7)	0.6840 (4)
C(25)	0.5705 (8)	0.9435 (7)	0.6495 (4)
C(26)	0.6709 (9)	0.9905 (8)	0.6736 (5)
C(27)	0.7723 (10)	1.0108 (9)	0.6407 (6)
C(28)	0.7751 (10)	0.9848 (9)	0.5845 (5)
C(29)	0.6765 (10)	0.9361 (8)	0.5593 (5)
C(210)	0.5733 (9)	0.9166 (8)	0.5917 (4)
C(211)	0.4077 (9)	0.9529 (7)	0.7916 (4)
C(212)	0.2979 (9)	0.9704 (8)	0.8215 (4)
C(213)	0.2971 (11)	0.9903 (8)	0.8801 (4)
C(214)	0.4072 (12)	0.9927 (8)	0.9099 (5)
C(215)	0.5170 (11)	0.9792 (8)	0.8825 (5)
C(216)	0.5162 (10)	0.9584 (8)	0.8245 (5)
C(217)	0.2413 (10)	1.0081 (8)	0.6069 (5)
C(218)	0.1720 (10)	0.9366 (8)	0.5859 (4)
C(219)	0.0846 (9)	0.9130 (8)	0.6249 (5)
C(220)	0.0978 (11)	0.9747 (10)	0.6737 (5)
C(221)	0.1989 (11)	1.0358 (8)	0.6610 (5)

Restricted Rotation of the Alkyne Ligand. The room-temperature ^{13}C NMR spectra of both **1a** and **1b** exhibit single carbonyl carbon resonances. Although in **1a** this could result from a rigid structure with equivalent carbonyl groups like that observed in the crystal structure, this is not true for **1b** and suggests in each case the probable rotation of the alkyne ligand about the Re–alkyne axis. In **1b** the spectra at −60 and −80 °C exhibit two equal intensity carbonyl carbon resonances, but the resonances for all other carbon atoms remain unperturbed. This is only consistent with a single frozen-out structure (ignoring enantiomers), and this must have the PhC_2Me ligand oriented parallel to the plane of the Cp ring as is observed for the Ph_2C_2 ligand in the crystal structure of **1a**. The CMe and CPh acetylenic carbon resonances could be unambiguously assigned from proton-coupled spectra.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Brüker WM-400 spectrometer at 400 and 100 MHz, respectively. Infrared spectra were measured on a Perkin-Elmer 983 spectrophotometer and Raman spectra with a Cary Model 81 with a Spectra-Physics Model 125 HeNe laser. Solvents were dried and distilled under nitrogen, and all operations were conducted under nitrogen. $CpRe(CO)_2(THF)$ was synthesized and isolated as previously described.[24]

Preparation of $CpRe(CO)_2(C_2Ph_2)$ (1a). Method 1. $CpRe(CO)_2THF$ (51 mg, 0.132 mmol) and a large excess of C_2Ph_2 (115 mg, 0.645 mmol) was added to 12 mL of hexanes and stirred vigorously for 4 h. Chromatography on Florisil with hexane as an eluant gave yellow $CpRe(CO)_2(C_2Ph_2)$ (19 mg, 30% yield): IR

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[22] Espiritu, A. A.; White, J. G. *Z. Kristallogr.* **1978**, *147*, 177.

[23] Molecules 1 and 2 also differ in a minor way in the orientation of the Cp ring with respect to the basal carbon atoms, as can be seen in Figure 2.

[24] Barrientos, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.

(hexane) 1980 (s), 1904 (s) cm^{-1} (ν(CO)); Raman (solid) 1848 cm^{-1} (ν(C≡C)); ^{1}H NMR ($CDCl_3$) δ 7.85–7.32 (m, Ph), 5.55 (s, Cp); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 204.5 (CO), 131.8, 131.6, 128.6, 127.6 (Ph), 88.2 (Cp), 81.7 (acetylenic carbons); mass spectrum, m/e (based on Re^{185} and Re^{187}) 484, 486 (M$^+$), 456, 458 (M – CO$^+$), 428, 430 (M – 2CO$^+$). Anal. Calcd: C, 51.95, H, 3.11. Found: C, 52.21; H, 3.26.

Method 2. $CpRe(CO)_3$ (130 mg, 0.336 mmol) and C_2Ph_2 (220 mg, 1.23 mmol) were added to 30 mL of hexanes in a quartz Carius tube under vacuum and irradiated with a 200-W Hanovia high-pressure mercury source. Chromatography on Florisil yielded $CpRe(CO)_3$ (colorless) and $CpRe(CO)_2(C_2Ph_2)$ (yellow) (18 mg, 11% yield).

Preparation of $CpRe(CO)_2(PhC_2Me)$ (1b). This compound was synthesized as in method 1 (above) using $CpRe(CO)_2$(THF) (100 mg, 0.259 mmol) and PhC_2Me (0.15 mL, ~1.2 mmol). $CpRe(CO)_2(PhC_2Me)$ was isolated, after chromatography, as an oily, yellow solid and identified by spectroscopy: IR (hexane) 1976 (s), 1899 (s) cm^{-1} (ν(CO)); ^{1}H NMR ($CDCl_3$) δ 7.33–7.61 (m, Ph), 5.40 (s, Cp), 2.75 (s, Me); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 204.9 (CO), 131.4, 128.3, 126.8 (Ph), 87.9 (Cp), 78.2 (CMe), 69.4 (CPh), 15.2 (Me) [in the ^{1}H-coupled spectrum, δ 78.2 (q, ^2J = 9 Hz), 69.4 (s), 15.2 (q, ^1J = 130 Hz); at –60 °C ^{13}C–^{1}H-coupled spectrum, δ 206.5 (s), 206.0 (s, CO), 132.6–126.2 (complex, Ph), 88.3 (^1J = 180 Hz, Cp), 78.9 (q, ^2J = 9 Hz, CMe), 69.3 (s, CPh), 15.9 (q, ^1J = 130 Hz, Me)]; mass spectrum, m/e 422, 424 (M$^+$), 394, 396 (M – CO$^+$), 366, 368 (M – 2CO$^+$).

Oxidative Stability of $CpRe(CO)_2(C_2Ph_2)$. The color of solid samples of $CpRe(CO)_2(C_2Ph_2)$ (yellow) remained unchanged after being left standing in air for 1 week, and they could then be dissolved to give essentially clean IR and NMR spectra. A solution of $CpRe(CO)_2(C_2Ph_2)$ in hexanes was left open to the air and periodically monitored by IR. No decomposition was noted in 12 h.

Thermal Stability of $CpRe(CO)_2(C_2Ph_2)$. A solution of $CpRe(CO)_2(C_2Ph_2)$ in isooctane was refluxed (99 °C) for 8 h, and no decomposition or loss of CO was noted by IR. A solution of $CpRe(CO)_2(C_2Ph_2)$ in THF was refluxed (66 °C) for 1 h, after which no starting material remained and no carbonyl containing products were apparent from the IR spectrum.

Reaction of $CpRe(CO)_2(C_2Ph_2)$ with Carbon Monoxide. $CpRe(CO)_2(C_2Ph_2)$ (1a) (15 mg, 0.039 mmol) was dissolved in 10 mL of hexanes in a Paar bomb and pressurized with CO (1200 psi, 82 atm). After 1 h, the pressure was released and an IR spectrum of the yellow solution revealed only CO bands due to 1a and none for $CpRe(CO)_3$ (2031, 1940 cm^{-1}).

Reaction of $CpRe(CO)_2(C_2Ph_2)$ with PPh_3. To a solution of $CpRe(CO)_2(C_2Ph_2)$ (15 mg, 0.039 mmol) in 6 mL of hexane, octane, or acetonitrile was added excess PPh_3 (20 mg, 0.076 mmol). As monitored by IR, no reaction was observed after 2 h. Me_3NO (6 mg, 0.080 mmol) was then added to the acetonitrile solution, but no reaction was noted after a further 2 h. The CH_3CN solution was refluxed for 5 h, but no loss of CO ligand was observed.

X-ray Structure Determination for $CpRe(CO)_2(C_2Ph_2)$ (1a). Data collected on an Enraf-Nonius CAD4-F diffractometer were corrected for Lorentz, polarization, and absorption errors and 3008 reflections were regarded as observed ($I \geq 3.0\sigma(I)$). Pertinent crystal and data collection parameters can be found in Table IV.

The three-dimensional Patterson synthesis was used to determine the coordinates of the Re atoms. Full matrix, least-squares refinement and electron-density difference syntheses revealed all remaining non-hydrogen atoms, and with isotropic temperature factors the structure refined to $R = 0.069$ and $R_w = 0.077$. At this point, the phenyl and cyclopentadienyl hydrogen atom positions were calculated (d(C–H) = 0.95 Å), assigned isotropic temperature factors equal to those of the parent carbon atoms, and included as fixed contributions in further refinement. All non-hydrogen atoms were assigned anisotropic temperature factors. The structure was refined by further cycles of full-matrix least squares until all shift-to-error ratios were less than 0.01. Final residuals were $R_F = 0.0295$ and $R_{wF} = 0.034$, and the goodness of fit was 1.17. For the final cycles, the weighting scheme used was $w = [\sigma(F_o)^2 + pF_o^2]^{-1}$. The value of parameter p (= 0.0004) was that for which the variation of the averaged $\sum\{w(|F_o| - |F_c|)\}^2$ with F_o and $(\sin \theta)/\lambda$ was observed to be minimum. The largest peaks in a final difference map were of height 0.56 (6) e Å^{-3} and were located close to the Re atoms. Neutral scattering factors with anomalous dispersion corrections for the nonhydrogen atoms were used.[25] Computer programs[26] were run on an in-house VAX 11-750. Positional parameters are listed in Table V.

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Registry No. 1a, 59676-03-8; 1b, 94458-44-3; $CpRe(CO)_2$THF, 59423-86-8; $CpRe(CO)_3$, 12079-73-1; Ph_2C_2, 501-65-5; PhC_2Me, 673-32-5.

Supplementary Material Available: Tables of the calculated mean planes and dihedral angles (Table VI), anisotropic thermal parameters (Table VII), calculated hydrogen atom coordinates (Table VIII), and the calculated and observed structure amplitudes (Table IX) (27 pages). Ordering information is given on any current masthead page.

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[25] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV, Tables 2.28, 2.31.

[26] Larson, A. C.; Gabe, E. J. "Computing in Crystallography"; Schenk, H., et al., Eds.; Delft University Press: Holland, 1978. Larson, A. C.; Lee, F. L.; LePage, Y.; Gabe, E. J. "The N.R.C. VAX Crystal Structure System"; Chemistry Division N.R.C.: Ottawa, Ontario, Canada.