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SYNTHESIS, STRUCTURE, AND PHOTOCHEMISTRY OF A RHENIUM(I) ENOLATE COMPLEX

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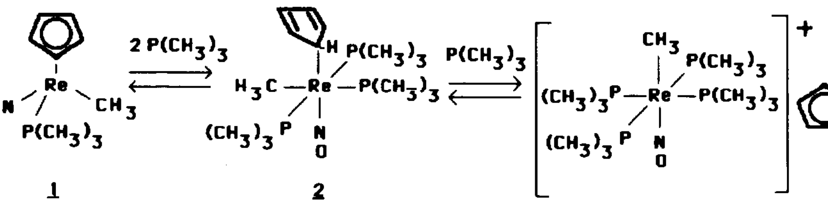
Summary

The rhenium(I) enolate complex *fac*-$(CO)_3(P(CH_3)_3)_2Re(OC(CH_3)C_5H_4)$ (**4**) was prepared from the reaction of $(\eta^5\text{-}C_5H_4C(O)CH_3)Re(CO)_3$ (**3**) with $P(CH_3)_3$. Compound **4** was characterized structurally in the solid state by X-ray crystallography and in solution by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Photolysis of **4** at 337 nm in CH_2Cl_2 solution cleaves the Re–O bond: smooth conversion to *fac*-$(CO)_3(P(CH_3)_3)_2ReCl$ (**5**) is observed with a quantum yield of 0.04.

Introduction

Ring-slippage reactions of the cyclopentadienyl (C_5H_5) ligand have been under intense investigation [1]. A particularly intriguing example is that reported by Casey, et al. [2], wherein conversion of an η^5- to an η^1- and even an η^0-bonded C_5H_5 ring occurs, as shown in eq. 1. Our interest in excited-state processes prompted us to prepare **3** as a precursor to compounds similar to **2**, which might exhibit photo-induced ligand elimination, resulting in a ring-slippage reaction.



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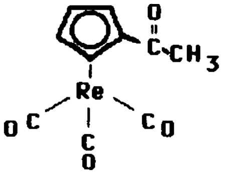
(1)

We report in this paper that reaction of **3** with $P(CH_3)_3$ does not yield the η^1 derivative analogous to **2**, but rather the novel rhenium(I) enolate complex **4**. This



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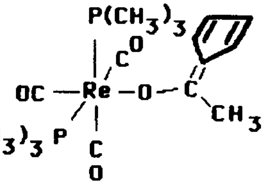

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compound has been characterized structurally in the solid state by X-ray crystallography and in solution by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. We also demonstrate that the compound undergoes efficient photo-induced Re–O bond cleavage: clean conversion of **4** to *fac*-$(CO)_3(P(CH_3)_3)_2ReCl$ (**5**) obtains with a quantum yield of 0.04.

Experimental

Materials and general procedures. Hexane, CH_2Cl_2, and $CHCl_3$ were purified by sequential washes with H_2SO_4 and aqueous $NaHCO_3$, followed by a drying treatment with $CaCO_3$; prior to use the three solvents were distilled under N_2 from Na, CaH_2, and P_2O_5, respectively. Gold Label benzene (Aldrich) was distilled from NaK alloy under N_2 before use. Trimethylphosphine was liberated from $[(CH_3)_3P/AgI]_4$ (Aldrich) by heating; the phosphine was always handled using a vacuum line with quantities determined by volume. Pentacarbonylrhenium bromide (Pressure Chemical) and $Eu(fod)_3$ (Aldrich) (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionanto) were used as received. Compound **5**, *fac*-$(CO)_3(P(CH_3)_3)_2ReCl$, was prepared by literature procedure [3] and recrystallized from ethanol; the compound was characterized by ^1H NMR spectroscopy [3], HRMS, and its electronic spectrum (CH_2Cl_2 solution: λ_{max} 290 nm; ε 2.1×10^3 M^{-1} cm^{-1}). The salt $Na[C_5H_4C(O)CH_3]$ was prepared by a literature procedure and stored in a N_2-filled glove bag [4]. All solutions were handled under N_2 in the dark.

Spectra. Infrared spectra were recorded on a Beckman Model 4230 spectrophotometer. Electronic spectra were obtained using a Cary 17D spectrophotometer. A Bruker WP 200 instrument was used for 200 MHz ^1H NMR spectra. A Bruker WP 500 instrument was used for 125.8 MHz ^{13}C and 202.5 MHz ^{31}P NMR spectra with chemical shifts referenced to internal $CDCl_3$ and external $P(C_6H_5)_3$, respectively. Mass spectra were acquired using a Kratos MS-80 instrument.

Preparation of $(\eta^5\text{-}C_5H_4C(O)CH_3)Re(CO)_3$ *(3) [5].* A 250-ml three-neck flask was filled in a N_2-filled glove bag with 3.1 g $Re(CO)_5Br$ (7.7 mmol), a three-fold excess of $Na[C_5H_4C(O)CH_3]$ (3.0 g, 23 mmol), and 50 ml of benzene. The flask was removed from the glove bag and the mixture was refluxed under N_2. The reaction was followed by monitoring the appearance of the carbonyl band at 1940 cm^{-1} due to **3** in the IR. After ca. 40 h, the reaction mixture was cooled and excess solvent removed under vacuum. The residue was dissolved in ether and washed thrice with water; the solvent was then removed on a rotary evaporator. The compound was dissolved in a minimum of CH_2Cl_2 and added to a silica gel column. Elution with CH_2Cl_2 gave two pale yellow bands. Examined by IR, the second band contained the desired material with a small quantity of impurity. After evaporation of the solvent, the product was sublimed under vacuum (10^{-3} torr; $> 60\,^\circ C$) to give **3**

(0.92 g, 32%) as a white solid, m.p. 75–76 °C (uncorrected). HRMS: m/e, calcd.: 377.9872 (M^+); found: 377.9902 (M^+) and calcd.: 321.9974 (M^+-2CO); found: 321.9955 (M^+-2CO). ^1H NMR ($CDCl_3$; 200 MHz): δ 5.98 (t, J 2.2 Hz, 2H), 5.40 (t, J 2.1 Hz, 2H), 2.34 (s, 3H). IR (CH_2Cl_2): 2030(s), 1940(s), 1690(s) cm^{-1}. UV-VIS (CH_2Cl_2): λ_{max} 267 nm; ε 4.4×10^3 M^{-1} cm^{-1}.

*Preparation of fac-$(CO)_3(P(CH_3)_3)_2Re(OC(CH_3)C_5H_4)$ (**4**).* A 35-ml reaction tube, fitted with a Teflon needle valve, was charged with 0.33 g (0.89 mmol) of **3**, 5 ml of dry hexane, and a stir bar in a N_2-filled glove bag and attached to a vacuum line. The solution was frozen with liquid N_2, evacuated, and thawed in three degassing cycles. An excess of $P(CH_3)_3$, 0.8 ml, was then introduced. The reaction tube was sealed and heated at 60–70 °C for 18 h with constant stirring. A yellow powder precipitated as the reaction progressed. Sometimes a red solid collected just above the solvent line; this was separated and discarded, but its appearance could be prevented by stirring. Excess solvent and $P(CH_3)_3$ were removed under vacuum, leaving **4** as a pale yellow solid (0.44 g, 93%), m.p. 157–159 °C (uncorrected). HRMS: m/e calcd.: 530.0752 (M^+); found: 530.0736 (M^+); calcd.: 502.0803 (M^+-CO); found: 502.0800 (M^+-CO); calcd.: 474.0854 (M^+-2CO); found: 474.0880 (M^+-2CO). ^1H NMR ($CDCl_3$; 200 MHz): δ 6.56 (m, 1H), 6.45 (m, 1H), 6.22 (m, 1H), 6.16 (m, 1H), 2.29 (s, 3H), 1.62 (m, J(PP) −66 Hz, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$; 125.8 MHz): δ 193, 192, $191._5$ (3CO), 184 (O-CCH_3), 125, 120, 119, 118, 115 ($OC(CH_3)C_5H_4$), 25 (CH_3), 18 (m, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 202.5 MHz), δ vs. H_3PO_4, ($P(C_6H_5)_3$ as an external standard): −17.5 (s). IR (CH_2Cl_2): 2030(s), 1940(s), 1905(s), 1515(s) cm^{-1}. UV-VIS (CH_2Cl_2): λ_{max} 337 nm; ε 3.1×10^4 M^{-1} cm^{-1}.

Crystallographic data. A single crystal of **4** was obtained by layering hexane on a CH_2Cl_2 solution of the complex. Preliminary examination showed the space group to be the uniquely determined orthorhombic *Pbca*. Unit cell parameters were obtained from least squares refinement based on the setting angles of 25 reflections with $2\theta\sim23°$. The crystal dimensions, unit cell parameters, and other crystal data are given in Table 1, as are details of the intensity measurements. Four standard reflections from diverse regions of the reciprocal space were measured every 50 reflections throughout data collection to monitor the long term stability. No significant trend was observed. The structure was solved by direct methods using the SHELXTL package. After all nonhydrogen atoms were located, partially refined electron density difference maps revealed that the trimethylphosphine ligands were disordered. The disordered ligands were modeled as idealized C_{3v} rigid groups (d[P–C] 1.82 Å) with the group occupancies being refined with appropriate constraints such that the sum of the occupancies of the major and minor orientations was required to be 1.0. The block-cascade least squares refinement of the structure was based on F_o using the reflections with $F_o>3\sigma(F_o)$. The final cycles of refinement treated all the atoms of the minor occupancy phosphines isotropically. Also, due to the short distances between the major and minor occupancy phosphorus atoms, the major occupancy phosphorus atoms were treated as isotropic atoms. All other nonhydrogen atoms were assumed to vibrate anisotropically. Due to the disorder, hydrogen atoms were not included on the phosphine methyl groups. All other hydrogen atoms were included as fixed contributors in idealized locations (d[C–H] 0.96 Å). The final refined values for the major group occupancies were 0.74(4) for P(1) and 0.83(2) for P(2). The final values of the discrepancy indices are

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION [a] FOR *fac*-$(CO)_3(P(CH_3)_3)_2Re(OC(CH_3)C_5H_4)$ (4)

Empirical formula	$C_{16}H_{25}O_4ReP_2$
Formula weight	529.5
Crystal dimensions	0.3×0.4×0.75
Temperature (K)	295
Cell parameters a (Å)	11.354(4)
b (Å)	15.237(4)
c (Å)	24.652(5)
Space group	*Pbca*
Z	8
Calculated density (g/cm^3)	1.65
Absorption coefficient (μ, cm^{-1})	59.4
Nicolet diffractometer [b]	P3/F
Scan type	Omega
Scan range (deg centered on $2\theta K_\alpha$)	1.0
Scan speed (deg/min)	2.5–29.3
Background/scan ratio	0.25
2θ limits (deg)	3.5–54.9
$\sin\theta/\lambda_{max}$	0.649
Unique data, theoretical	4874
$F_o > 3\sigma(F_o)$	2913
p; weight $= [\sigma^2(F) + p^2F^2]^{-1}$	0.03
Discrepancy indices, R_1	0.066
R_2	0.072
Goodness of fit	1.33
Observation/variable ratio	13.8

[a] Method similar to K.J. Haller and J.H. Enemark, Inorg. Chem., 17 (1978) 3552. Scattering factor tables from International Tables for X-ray Crystallography, Kynoch Press: Birmingham England, 1974; vol. IV.
[b] Diffractometer equipped with a graphite-monochromated Mo-K_α radiation source.

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o| = 0.066$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w(F_o)^2)]^{1/2} = 0.072$. The final electron density difference map had peaks near the rhenium atom and near the phosphorus atoms of ~ 0.75 e/Å^3 but was otherwise featureless. Final atomic parameters are reported in Table 2. Anisotropic thermal parameters, calculated hydrogen atom positions, and a listing of $10|F_o|$, $10|F_c|$, and $\sigma(F_o)$ are included as supplementary material.

Photochemistry. Bulk photolysis of **4** was accomplished with a broad-band output blacklight (~ 335–380 nm), an Osram HBO 200-W super high pressure Hg lamp in an Oriel Model 7292 housing, or a Molectron UV-12 N_2 laser (337 nm). The photolysis was monitored by ^1H NMR spectroscopy; typically, 15 mg of **4** was dissolved in 0.5 ml of CD_2Cl_2 or $CDCl_3$ and photolyzed in a 1.0 mm pathlength quartz cell. Periodically, the sample was transferred from the cell to an NMR tube by syringe in a glove bag and its spectrum recorded. The principal nonvolatile Re-containing product is **5**, which was isolated by solvent removal under vacuum. The electronic, IR, and ^1H NMR spectra agreed with those of a sample of **5** prepared by literature procedure [3]. The volatile organic fragment 1-acetyl-1,3-cyclopentadiene (**6**) was characterized by its ^1H NMR spectrum, which matched that of an authentic sample prepared by literature procedure [6]. Moreover, addition

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR 4

Atom	x	y	z	U^{a}
Re	1572(1)	2015(1)	1221(1)	62(1)*
C(1)	1129(12)	2797(7)	648(5)	78(5)*
O(1)	966(9)	3292(6)	314(4)	113(5)*
C(2)	3076(16)	2562(11)	1215(6)	106(7)*
O(2)	3995(12)	2867(8)	1223(5)	159(8)*
C(3)	906(17)	2856(9)	1750(6)	115(8)*
O(3)	581(15)	3372(9)	2047(5)	169(8)*
O(4)	40(7)	1198(5)	1265(3)	62(3)*
C(4)	−1023(12)	1223(8)	1104(4)	64(4)*
C(5)	−1790(11)	520(9)	1208(4)	68(5)*
C(6)	−1503(12)	−263(9)	1469(5)	74(5)*
C(7)	−2514(13)	−768(9)	1493(5)	83(5)*
C(8)	−3438(14)	−314(11)	1236(5)	95(6)*
C(9)	−3014(11)	446(9)	1049(5)	79(5)*
C(10)	−1421(11)	2051(8)	811(6)	84(6)*
P(1)	2083(10)	929(4)	499(5)	62(2)
C(11)	1642	−204	613	93(10)*
C(12)	3613	803	294	118(12)*
C(13)	1368	1173	−144	143(15)*
P(2)	2274(5)	1092(5)	1975(3)	79(2)
C(14)	3682	540	1886	165(13)*
C(15)	1341	203	2215	125(10)*
C(16)	2522	1716	2593	247(22)*
P(1B)	2301(28)	915(11)	627(14)	61(5)
C(11B)	2030	−222	813	0(13)
C(12B)	3810	868	381	0(13)
C(13B)	1473	1012	−3	0(13)
P(2B)	2178(21)	1360(19)	2095(10)	61(5)
C(14B)	2769	275	1948	0(27)
C(15B)	3437	1902	2404	0(27)
C(16B)	1248	1142	2680	0(27)

[a] Thermal parameters marked with * are equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. The trimethylphosphine ligands were treated as rigid groups with the phosphorus atoms as pivot atoms. The errors on the group origin positions are given with the phosphorus atoms.

of $\mathrm{Eu(fod)_3}$ to a $CDCl_3$ solution of **6** yielded ^{1}H NMR spectral shifts consistent with the presence of only this isomer of **6**.

Quantum yields. Quantum yields were determined using the N_2 laser or Hg lamp. When using the Hg lamp, its output was passed through a water filter, a Corning 121 cutoff filter for removal of visible radiation, and a Corning 334-nm interference filter; the absorbed intensity is 0.18 mW. A quartz microscope slide served as a beam splitter, reflecting about 15% of the monochromatized light into an EG&G Model 550-1 radiometer. The radiometer's output was monitored by a Varian 9176 strip-chart recorder; an Apple IIe microcomputer was used to calculate the photon flux by integrating the resulting power-time curve. Quantum yield employing the N_2 laser, 7.5 mW output, involved use of a Scientech Model 362 integrating radiometer. Quantum yield measurements were made on 1.0 m*M* CH_2Cl_2 or $CHCl_3$ solutions of **4**, using 0.4 ml of the solution in 1.0 mm pathlength quartz cells; the solutions were prepared and sealed in a N_2-filled glove bag. For obtaining quantum yields in the presence of $NaHCO_3$, the solid was first washed with hexane and then added (11–13 mg; 0.13–0.16 mmol) to the quartz cell. Acquisition of quantum yields with CO- or O_2-saturated solutions was accomplished by handling the sample under a CO or O_2 atmosphere, respectively. Quantum yields for the disappearance of **4**, ϕ_d, were determined by monitoring the decline in the absorption band at 337 nm with total conversion of $\leq 25\%$. Good linearity was found, including extrapolation to zero conversion at zero time. Values of ϕ_d are based on at least three complete sets of data with five data points per set. The quantum yields are uncorrected for reflective losses; reproducibility was ±15%.

*Reaction of **4** with HCl.* In a N_2-filled glove bag, a flask was filled with 30 mg **4** (0.057 mmol) and 5 ml CH_2Cl_2 or $CHCl_3$. Gaseous HCl (Matheson) was then bubbled through the solution for 3 h. After evaporation of the solvent under N_2, a ^1H NMR spectrum taken in $CDCl_3$ confirmed that **4** had been converted to **5**.

Solvent photolysis. In a glove bag, a 1.0 mm pathlength quartz cell was filled with 0.4 ml CH_2Cl_2. The cell was exposed to 337 nm irradiation for periods of up to 1000 s. The sample was then returned to the glove bag where 0.9 μl of a 60 mM CH_2Cl_2 solution of **4** was added. An electronic spectrum of the solution matched that expected for a solution of **4**.

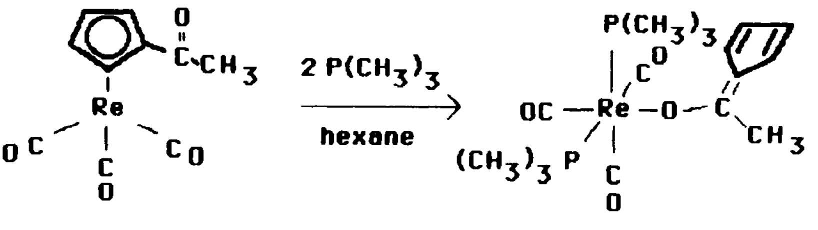
*Thermal reactivity of **4**.* A reaction tube was filled with 5 ml of toluene and 20 mg of **4** in a N_2-filled glove bag and sealed with a Teflon needle valve. The vessel was heated in an oil bath for several days at 70 °C. After the reaction mixture was returned to room temperature, the solvent was removed under vacuum. No product was observed by ^1H NMR spectroscopy in $CDCl_3$ other than **3**. No reaction of **4** was observed after boiling in CH_2Cl_2 or in toluene below 50 °C for 2 days.

Results and discussion

In sections below we discuss the synthesis of **4**, its solid-state and solution structural features, and its photochemistry.

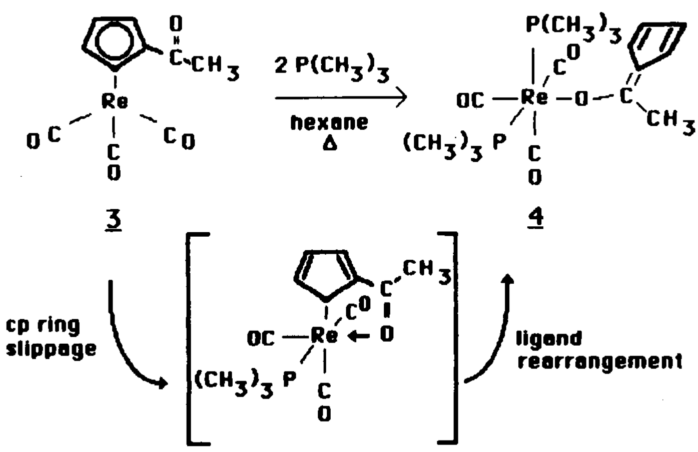
Synthesis

As shown in eq. 2, **3** is quantitatively converted to **4** simply by heating with



3 **4** (2)

$P(CH_3)_3$ in hexane solution. Production of the O-bonded enolate, established crystallographically (vide infra), is intriguing. While known for the Group IV transition metals [7,8], oxygen-bonded enolates are rare for later transition elements (excluding, of course, the ubiquitous β-diketonate complexes). Some examples with palladium(II) were reported; these species were initially postulated as intermediates



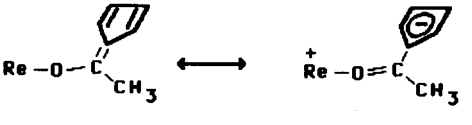
SCHEME 1. A possible mechanism for the transformation of 3 to 4.

in the reactions of silyl enol ethers with palladium(II) to form unsaturated ketones and aldehydes [9]. For Re, we are aware of a C-bonded enolate [10] and a ketene formed by insertion of CO into an (η^1-C_5H_5)–Re bond [11].

Mechanistically, production of the enolate is surprising given the conversion of eq. 1 wherein an η^5-C_5H_5 ligand becomes η^1-bonded. Our results do not preclude such a process: the η^1-bonded species may well be an intermediate in enolate formation, as shown in Scheme 1. Favoring the formation of the η^1-intermediate shown are the conjugation of the acetyl substituent with the ring; the relatively unstrained five-membered chelate structure; and the smooth conversion afforded to the planar enolate ligand (vide infra) of **4**. Experimental support for the η^1-intermediate is the observation that **4** reverts to **3** at 70 °C over a period of days, paralleling the more facile conversion of **2** back to **1** [2,12]. Although an intramolecular ligand rearrangement mechanism is outlined in Scheme 1, our results do not exclude the possibility of a dissociative mechanism involving an η^0-C_5H_5 species [2].

Structural features

A single-crystal X-ray diffraction study of **4** established the solid-state structure shown in the ORTEP drawing of Fig. 1. A least-squares plane through the enolate ligand [13] and selected bond lengths and angles, Table 3, clearly demonstrate that a *facial* isomer with a planar oxygen-bonded enolate ligand has been produced. The structure suggests that the resonance structures shown below are important in describing the ligand and may contribute to the unusual stability of **4**. This is



supported by the nearly equivalent C–C bond lengths in the ring, the ligand planarity (within the accuracy of the structure), and the summation of the angles around C(4) and C(5) to 360.0 and 359.9, respectively, characteristic of sp^2-hybridized carbon atoms.

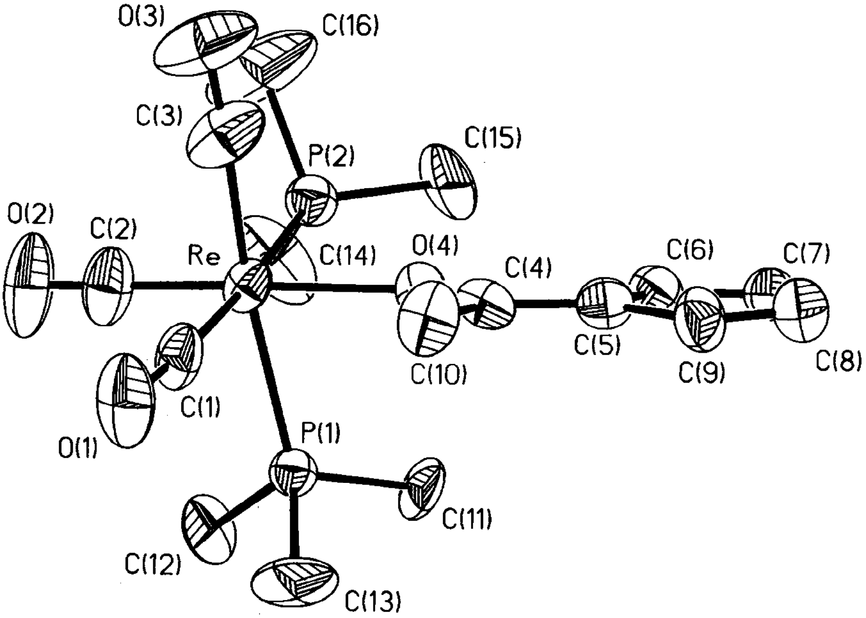


Fig. 1. The molecular crystal structure of **4** (hydrogen atoms omitted for clarity).

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR **4**

Re–C(1)	1.917(12)	Re–C(2)	1.900(18)
Re–C(3)	1.978(15)	Re–O(4)	2.141(8)
Re–P(1)	2.500(11)	Re–P(2)	2.461(6)
C(1)–O(1)	1.132(16)	C(2)–O(2)	1.143(23)
C(3)–O(3)	1.137(20)	O(4)–C(4)	1.271(16)
C(4)–C(5)	1.404(18)	C(4)–C(10)	1.521(18)
C(5)–C(6)	1.395(18)	C(5)–C(9)	1.449(18)
C(6)–C(7)	1.383(20)	C(7)–C(8)	1.408(21)
C(8)–C(9)	1.335(21)		
C(1)–Re–C(2)	87.5(6)	C(1)–Re–C(3)	89.0(6)
C(2)–Re–C(3)	93.7(7)	C(1)–Re–O(4)	100.7(4)
C(2)–Re–O(4)	170.2(5)	C(3)–Re–O(4)	91.9(5)
C(1)–Re–P(1)	86.9(4)	C(2)–Re–P(1)	94.3(5)
C(3)–Re–P(1)	170.8(6)	O(4)–Re–P(1)	80.8(3)
C(1)–Re–P(2)	175.4(4)	C(2)–Re–P(2)	88.1(5)
C(3)–Re–P(2)	89.8(5)	O(4)–Re–P(2)	83.9(2)
P(1)–Re–P(2)	94.8(3)	Re–C(1)–O(1)	173.7(12)
Re–C(2)–O(2)	177.5(14)	Re–C(3)–O(3)	175.8(16)
Re–O(4)–C(4)	137.6(7)	O(4)–C(4)–C(5)	120.6(11)
O(4)–C(4)–C(10)	117.1(11)	C(5)–C(4)–C(10)	122.3(12)
C(4)–C(5)–C(6)	126.3(12)	C(4)–C(5)–C(9)	127.2(12)
C(6)–C(5)–C(9)	106.4(12)	C(5)–C(6)–C(7)	107.5(12)
C(6)–C(7)–C(8)	109.0(12)	C(7)–C(8)–C(9)	108.3(13)
C(5)–C(9)–C(8)	108.7(12)	Re–P(1)–C(11)	117.0(2)
Re–P(1)–C(12)	119.3(2)	Re–P(1)–C(13)	112.4(3)
Re–P(2)–C(14)	117.3(1)	Re–P(2)–C(15)	118.8(1)
Re–P(2)–C(16)	112.6(2)		

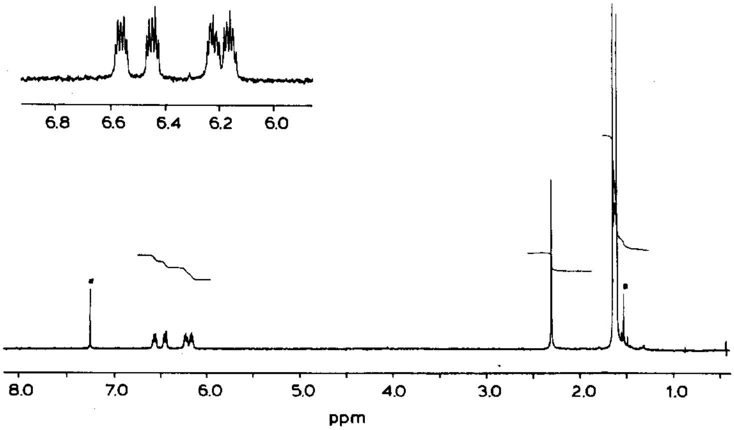


Fig. 2. The ^1H NMR spectrum of 4 in $CDCl_3$.

Compound **4** was characterized in halocarbon solution by IR and NMR spectroscopy and shown to have a structure consistent with that determined crystallographically. The IR spectrum exhibited three strong bands in the terminal carbonyl region (2030, 1940, and 1905 cm^{-1}) and a band at 1515 cm^{-1} assignable to the enolate ligand [8,11].

The ^1H NMR spectrum of **4** in $CDCl_3$ consists of four multiplets each of unit intensity, as shown in Fig. 2. These resonances can be assigned to the protons on the fulvene ring; the pattern is typical of fulvene systems [14]. A $X_9AA'X'_9$ pattern at δ 1.62, assigned to the phosphine protons, permits determination of J(PP) as being -66 Hz; the magnitude of the coupling constant is consistent with a *cis* arrangement of phosphine ligands [12,15,16]. A substituted fulvene moiety was also evidenced by the $^{13}C\{^1H\}$ NMR spectrum: a peak is observed at δ 184 and assigned to the exocyclic C atom based on related compounds [14]. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ -17.5 vs. H_3PO_4 for the equivalent P nuclei.

Photochemistry

The electronic spectrum of **4** in CH_2Cl_2 is shown in Fig. 3. Dominating the spectrum is an intense (ε 3.1×10^4 M^{-1} cm^{-1}) band with its maximum at 337 nm. Irradiation into this band caused a decrease in absorbance and the appearance of a new band at 285 nm. The course of the reaction is illustrated in Fig. 3 and appears to be a smooth conversion based upon the presence of isosbestic points at 243, 295, and 385 nm.

The photolysis was repeated on a larger scale in $CDCl_3$ so that its course could be followed by ^1H NMR spectroscopy. The spectral evolution is shown in Fig. 4, following which the sample was separated into its nonvolatile and volatile fractions. A multiplet at δ 1.61 characterized the nonvolatile component. This species was determined by mass spectral peak match to be *fac*-$(CO)_3(P(CH_3)_3)_2ReCl$ (**5**), signifying that the Re–O bond has been cleaved by photolysis; an independently prepared sample of **5** confirmed the product assignment. The conversion of **4** to **5**

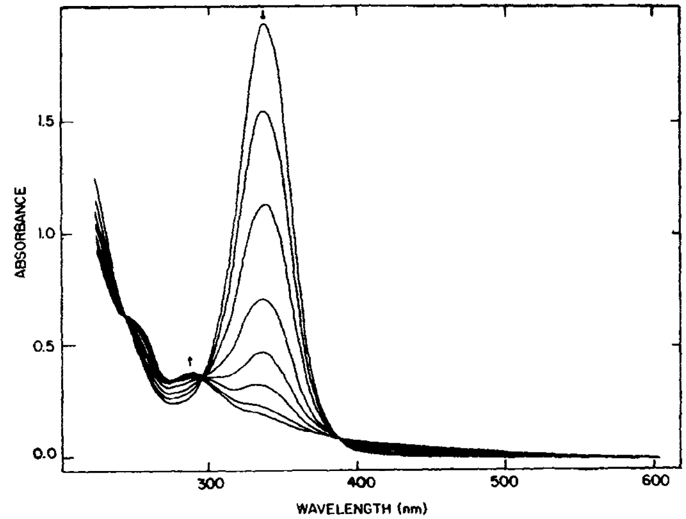
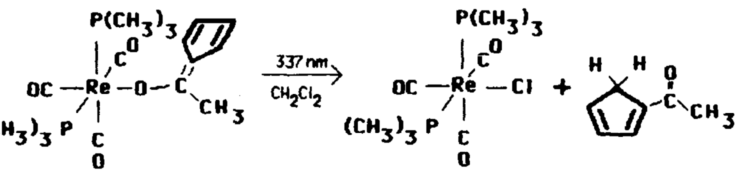


Fig. 3. The photoreaction of 4 monitored by electronic spectroscopy in CH_2Cl_2. The curves shown correspond to successive 4 min photolysis periods using 334 nm excitation from a high-pressure Hg lamp.

(eq. 3) is nearly quantitative. Eventually, however, the photoreactivity of 5 is



4 **5** **6**

(3)

apparent: long-term photolysis leads to the triplet observed at δ 1.72 (last spectrum of Fig. 4).

The volatile portion of the photolysate accounts for the remaining peaks observed by ^1H NMR spectroscopy during photolysis. Peaks at 7.34(m), 6.75(m), 6.60(m),

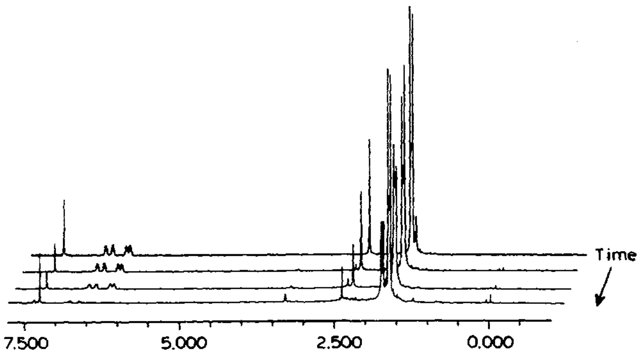


Fig. 4. The photoreaction of 4 in $CDCl_3$, monitored by ^1H NMR spectroscopy, at 0, 10, 30, and 100% conversion. The spectra are offset for clarity.

3.29(q), and 2.37(s) ppm in a ratio of 1/1/1/2/3 match those of an independently prepared sample of 1-acetyl-1,3-cyclopentadiene (**6**) [6]. A dark red color typically observed in long-term photolyses of **4** may result from decomposition of **6**.

It is noteworthy from a mechanistic standpoint that the metal and organic products are derived from halogen and hydrogen abstraction, respectively. This observation suggests that HCl may be involved in the reaction. Indeed, in the dark, gaseous HCl reacts with **4** to yield **5** and **6**. However, two control experiments argue against the involvement of HCl in the photoreaction. First, the quantum yields, ϕ_d, for the disappearance of **4** in CH_2Cl_2 and $CHCl_3$, 0.04 and 0.10, respectively, are unaffected by the presence of an insoluble base, $NaHCO_3$. Second, direct photolysis of either solvent with subsequent addition in the dark of **4** left the complex intact based on the electronic spectrum of the solution.

Quantum yield measurements made in CH_2Cl_2 solution in the presence of excess trimethylphosphine (10 to 100 equivalents present) and in the presence of CO and O_2 (saturated solutions of each gas) did not affect ϕ_d. These results suggest that Re–O bond cleavage is the primary photoprocess in this system.

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References

1 J.M. O'Connor and C.P. Casey, Chem. Rev., accepted.

2 C.P. Casey, J.M. O'Connor and K.J. Haller, J. Am. Chem. Soc., 107 (1985) 1241.

3 R.H. Reimann and E. Singleton, J. Organomet. Chem., 59 (1973) 309.

4 W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.

5 An alternate route to **3** with similar overall yield has been reported: E.O. Fischer and W. Fellman, J. Organomet. Chem., 1 (1963) 191.

6 G. Grundke and H.M.R. Hoffmann, J. Org. Chem., 46 (1981) 5428.

7 M.D. Curtis, S. Thanedar and W.M. Butler, Organometallics, 1 (1984) 1855.

8 K.H. Theopold, P.N. Becker and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 5250.

9 Y. Ito, M. Nakatsuka, N. Kise and T. Saegusa, Tetrahedron Lett., 21 (1980) 2873.

10 J.J. Doney, R.G. Bergman and C.H. Heathcock, J. Am. Chem. Soc., 107 (1985) 3724.

11 C.P. Casey and J.M. O'Connor , J. Am. Chem. Soc., 105 (1983) 2919.

12 C.P. Casey, J.M. O'Connor, W.D. Jones and K.J. Haller, Organometallics, 2 (1983) 535.

13 The equation of the least squares plane (crystal coordinates) is $-2.962x + 6.337y + 21.476z = 3.454$; deviations of atoms from the plane (Å) are O(4), 0.010; C(4), −0.005; C(5), 0.000; C(6), −0.020; C(7), 0.011; C(8), 0.021; C(9), −0.025; C(10), 0.008; Re, −0.019. The Re atom was not included in the calculation.

14 R. Hollenstein, W. von Philipsborn, R. Vögeli and M. Neuenschwander, Helv. Chim. Acta, 56 (1973) 847.

15 R.D. Bertrand, F.B. Ogilvie and J.G. Verkade, J. Am. Chem. Soc., 92 (1970) 1908.

16 J.G. Verkade, Coord. Chem. Rev., 9 (1972) 1.