Equilibrium between η^2-(*o*-Ethynylbenzoyl)rhenium Complexes and Rhenium Isobenzofuryl Carbene Complexes and Subsequent Reactions of Isobenzofuryl Carbene Complexes

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Thermal rearrangements of η^2-(*o*-ethynylbenzoyl)-Re complexes **2** produced isobenzofuryl-Re carbene complexes **3**. This reaction might proceed via nucleophilic attack of the carbonyl oxygen on the Re-bound alkyne or might proceed through a [1.5,1] Re shift followed by an electrocyclic ring closure. The two species, alkyne complex **2** and carbene complex **3**, were observed at equilibrium. Isobenzofuryl carbene complexes **3** were characterized by ^{1}H and ^{13}C NMR spectroscopy and by trapping via Diels−Alder reactions with DMAD. Air oxidation of the equilibrium mixtures of **2** and **3** led to oxidation of the isobenzofuryl carbene complexes **3** to unexpected Re η^2-ketone complexes **5**. Studies with ^{17}O-labeled dioxygen are consistent with oxygen addition to the isobenzofuran followed by rearrangement of the resulting endoperoxide that involves movement of the furan oxygen to the η^2-ketone site in **5**.

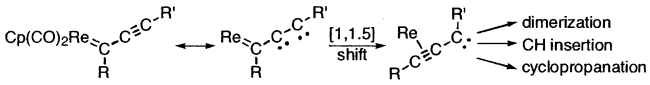
Introduction

Our recent studies of rhenium alkynylcarbene complexes demonstrated high reactivity at the remote alkyne carbon center. We have observed (1) dimerization of alkynylcarbene complexes by coupling at the remote alkyne carbon to give enediyne complexes,[1] (2) insertions of the remote alkyne carbon into the CH bond of a Cp* ligand,[1a,2] and (3) intramolecular cyclopropanation by addition of the remote alkyne carbon to a pendant alkene.[1a] All three reactions involve a net [1,1.5] rhenium migration to give rhenium alkyne complexes. These three transformations suggest emerging "free carbene" reactivity at the remote carbon of Re alkynyl carbene complexes (Scheme 1). A [1,1.5] rhenium shift would generate an alkyne complex adjacent to a center with "free carbene" character and reactivity.

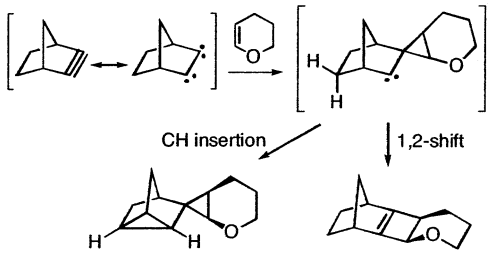
Strained alkynes sometimes react as formal dicarbenes. Alkyne ring strain favors a dicarbene resonance formulation with bent geometry at both carbons. Support for this dicarbene reactivity comes from thermal formation of [2+2] cycloadducts from reaction of cyclopentynes with alkenes, a reaction atypical of unstrained alkynes.[3] Gilbert and Laird recently observed dicarbene reactivity of norbornyne (Scheme 2).[4] When this highly strained alkyne was generated by lithiation of 2,3-dibromonorbornene in the presence of dihydropyran, products were obtained that could best be explained by dicarbene reactivity. It was proposed that one carbon of the dicarbene added to the double bond of the dihydropyran forming a cyclopropane adjacent to a carbene. This carbene intermediate then reacted through two pathways: (1) insertion into a CH bond to form a nortricyclene and (2) ring expansion by a [1,2] shift giving the [2+2] cycloadduct.

We wondered whether an alkyne bound to rhenium might also be able to react as a dicarbene. A [1.5,1] rhenium shift leading to a metal carbene complex might provide the impetus for emergence of "free carbene" character at the adjacent carbon (Scheme 3). This process is the reverse of the [1,1.5] rhenium shifts of

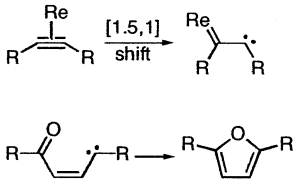
Scheme 1



Scheme 2



Scheme 3



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(1) (a) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771. (b) Casey, C. P.; Kraft, S.; Powell, D. R. *Organometallics* **2001**, *20*, 2651. (c) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584.

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(3) (a) Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495. (b) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885.

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10.1021/om040063g CCC: $27.50
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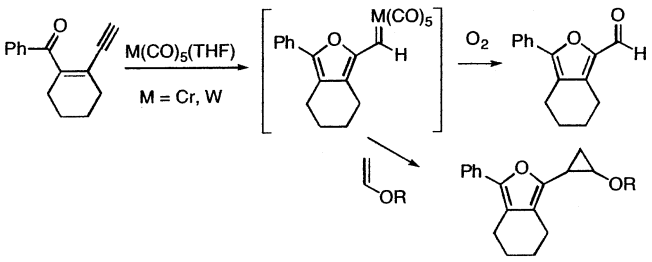
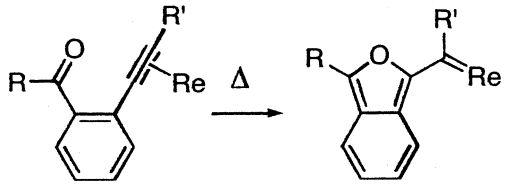
Scheme 4



Scheme 5



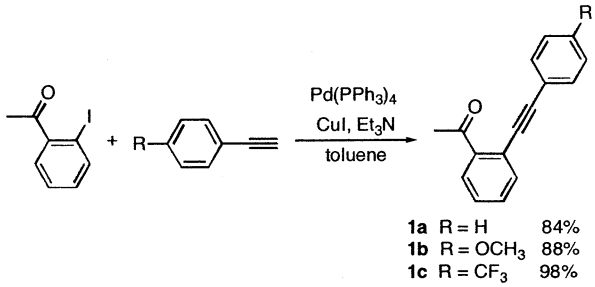
alkynylcarbene complexes previously studied in our group.

In searching for additional facile methods other than dimerization, CH insertion, and cyclopropanation for trapping a carbene, we turned our attention to the well-known 6π electrocyclic ring closing rearrangements of 4-oxabutadienylcarbenes to furans (Scheme 3).[5]

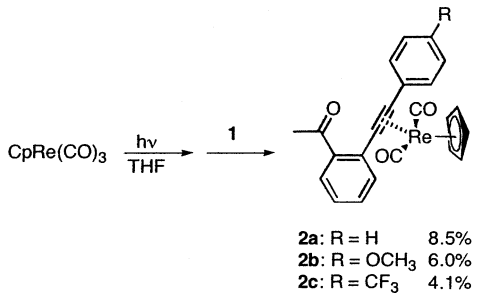
Reaction of *cis*-2-penten-4-yn-1-ones with $M(CO)_5$·THF led to the formation (2-furyl)carbene complexes, which were subsequently oxidized to furfurals by dioxygen (Scheme 4).[6,7] In related work, reaction of *cis*-2-penten-4-yn-1-ones with electron-rich alkenes in the presence of catalytic amounts of $M(CO)_5$·THF produced (2-furyl)cyclopropanes.[8] The authors suggested that the (2-furyl)carbene complex intermediates were formed by coordination of the metal to the alkyne followed by nucleophilic attack of the carbonyl on the complexed alkyne.[6,8] However, alkyne complexes were not observed, presumably due to rapid cyclization. Since weak nucleophiles do not attack Re alkyne complexes, we suggest consideration of an alternative pathway involving a [1.5,1] Re shift to give an intermediate with "free carbene" reactivity which then undergoes cyclization to a furan.

Since isobenzofurans have diminished aromaticity relative to furans, we hypothesized that switching from *cis*-2-en-4-yn-1-one complexes to 2-alkynylphenyl ketone complexes would lead to kinetically slower cyclization to isobenzofurylcarbene complexes and thermodynamically more stable rhenium alkyne complexes (Scheme 5). We hoped that the higher energy transition state leading to the isobenzofuran would slow conversion of the alkyne complex to the furylcarbene complex and that the greater relative stability of the alkyne complex might allow its direct observation or isolation.[9]

Scheme 6



Scheme 7



Here we report successful isolation of Re 2′-(arylethynyl)acetophenone complexes and their slow equilibration with Re isobenzofurylcarbene complexes. The isobenzofurylcarbene complexes were directly observed in solution by spectroscopy and were trapped by Diels–Alder reaction with dimethyl acetylenedicarboxylate and by reaction with molecular oxygen.

Results and Discussion

Synthesis of Alkyne Complexes. 2′-(Arylethynyl)-acetophenones (**1a**–**c**) were synthesized in very good yield (84–98%) via palladium-catalyzed Sonogashira couplings of 2′-iodoacetophenone with the appropriately substituted terminal alkynes (Scheme 6). The three alkynes were purified by flash column chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy and by HRMS.

$Cp(CO)_2$Re-alkyne complexes **2a**–**c** were prepared in low yield (4–8%) by reaction of 2–6 equiv of alkynes **1a**–**c** with $CpRe(CO)_2$(THF), which was generated by photolysis of $CpRe(CO)_3$ in THF under a continuous nitrogen purge (Scheme 7). Re-alkyne complexes **2a**–**c** were isolated as air-stable compounds by preparative TLC. The low yields of Re alkyne complexes **2a**–**c** are attributed to incomplete photolysis (~65% by IR spectroscopy) of $CpRe(CO)_3$ and rearrangement of **2a**–**c** to isobenzofurylcarbene complexes both during the alkyne complex synthesis and during TLC purification on silica gel.

Rhenium alkyne complexes were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and by HRMS. The ^{1}H NMR spectra of rhenium alkyne complexes **2a**–**c** were similar to those of the free ligands **1a**–**c**, except that in each case the methyl ketone resonance was shifted 0.4–0.5 ppm to lower frequency in the alkyne complex. The $Re(CO)_2$ group gave rise to two ^{13}C NMR resonances between δ 204 and 205 for complexes **2b** and **2c** and to a single broad resonance at δ 205.5 for **2a**. Slow rotation of the alkyne ligand renders the $Re(CO)_2$

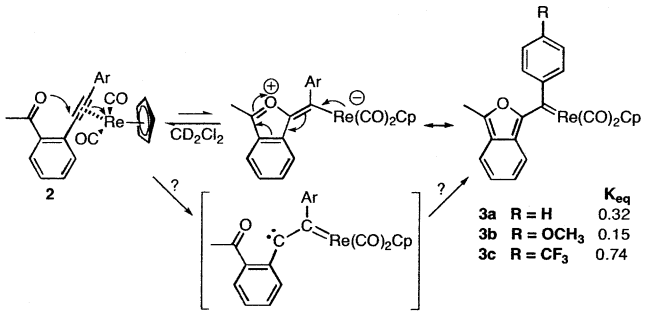
(5) (a) Tomer, K. B.; Harrit, N.; Rosenthal, I.; Buchardt, O.; Kumler, P. L.; Creed, D. *J. Am. Chem. Soc.* **1973**, *95*, 7402. (b) Padwa, A.; Akiba, M.; Chou, C. S.; Cohen, L. *J. Org. Chem.* **1982**, *47*, 183. (c) Nakatani, K.; Adachi, K.; Tanabe, K.; Saito, I. *J. Am. Chem. Soc.* **1999**, *121*, 8221.

(6) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228.

(7) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814.

(8) (a) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260. (b) Miki, K.; Yokoi, T.; Nishino, F.; Kato, Y.; Washitake, Y.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 1557.

Scheme 8



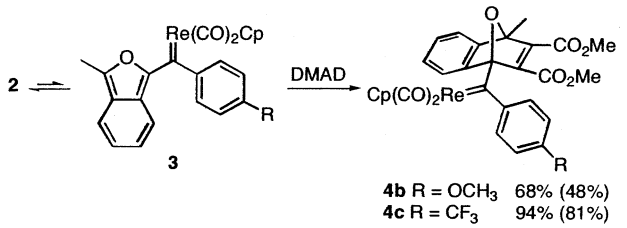
diastereotopic.[10] The ^{13}C NMR resonances of the alkyne carbons of **2a**−**c** (δ 79.0−91.0) are shifted 4−8 ppm to lower frequency relative to the resonances of the free alkynes **1a**−**c** (δ 87.5−95.4).

Equilibrium between Alkyne Complexes and Isobenzofuryl Carbene Complexes. When a solution of alkyne complex **2a** was heated at 38 °C, ^1H NMR spectroscopy revealed the slow formation of a new species which was shown to be isobenzofuryl carbene complex **3a** (Scheme 8). After 5 days ($\sim 20 \times t_{1/2}$), an equilibrium between **2a** and **3a** (76:24, $K_{eq} = 0.32$) was established. No attempt was made to isolate **3a** due to its extreme air sensitivity, its small fraction at equilibrium, and its relatively rapid rate of reequilibration with **2a**.

3a was characterized by ^1H and ^{13}C NMR spectroscopy of the equilibrium mixture of **2a** and **3a**. The resonances of the four isobenzofuran protons appeared at δ 7.08, 6.90 (m, 2H), and 6.80; due to lesser aromaticity of the isobenzofuran ring, these resonances are at lower frequency than typical aromatic resonances (δ 7.3−7.6). In the ^{13}C NMR spectrum, a carbene resonance was observed at δ 245.0 and two high-frequency resonances at δ 162.7 and 161.3 were seen for the furan carbons adjacent to oxygen.[11] The ^{13}C resonance for the methyl carbon on the isobenzofuran appeared at δ 15.1, which is 15 ppm to lower frequency than a methyl ketone resonance.

The methoxy-substituted alkyne complex **2b** was synthesized in the hope that the electron-donating methoxy group might selectively stabilize the isomeric carbene complex **3b** and give rise to more of **3b** at equilibrium. However, upon sitting at room temperature for 3 days, **2b** gave an equilibrium mixture containing even less of isobenzofuryl carbene complex **3b** (**2b**:**3b** = 87:13, $K_{eq} = 0.15$) (Scheme 8). Due to the low equilibrium concentration of **3b** relative to **2b** and to overlap of isobenzofuryl proton resonances with resonances of the protons of **2b** ortho to methoxy, full characterization of **3b** was not possible. **3b** was identified and monitored by ^1H NMR resonances at δ 5.26 (Cp), 3.86 (OMe), and 2.20 (Me).

Scheme 9



We next turned to an electron-withdrawing group in an effort to observe higher equilibrium concentrations of an isobenzofuryl carbene complex and synthesized the CF_3-substituted alkyne complex **2c**. After heating for 3 days at 38 °C in CD_2Cl_2, an equilibrium was established between **2c** and isobenzofuryl carbene complex **3c**. The electron-withdrawing substituent shifted the equilibrium toward the isobenzofuryl carbene complex isomer (**2c**:**3c** = 57:43, $K_{eq} = 0.74$). The ^1H and ^{13}C NMR spectra of **3c** were similar to those of **3a** and provided evidence for the isobenzofuryl carbene structure. Low-frequency aromatic resonances at δ 7.13, 7.05 (m, 2H), and 6.83 were observed for the four isobenzofuran protons. The carbene carbon resonance of **3c** appeared at δ 240.9,[12] and the resonances for the furyl carbons adjacent to oxygen appeared at characteristically high frequencies (δ 164.9 and 162.2).

The influence of solvent polarity on the equilibrium between alkyne and isobenzofuryl carbene complexes was briefly investigated. The equilibrium between **2a** and **3a** shifted toward isobenzofuryl carbene complex **3a** in solvents of lower dielectric constant [$K_{eq} = 0.32$ in CD_2Cl_2 ($\epsilon = 8.9$); $K_{eq} = 0.50$ in $CDCl_3$ ($\epsilon = 4.7$); $K_{eq} = 0.75$ in toluene-d_8 ($\epsilon = 2.4$)]. Similarly, the **2c**:**3c** equilibrium shifted toward **3c** in less polar solvents [$K_{eq} = 0.74$ in CD_2Cl_2; $K_{eq} = 1.62$ in C_6D_6 ($\epsilon = 2.3$)]. This solvent dependence is attributed to the greater stabilization of the more polar ketone functional group of **2** by solvents of higher dielectric constant than of the less polar isobenzofuran ring of **3**.

Trapping of Isobenzofuryl Carbene Complexes with DMAD. Since isobenzofurans are very reactive toward Diels−Alder dienophiles, we sought to trap the isobenzofuryl carbene complex with dimethyl acetylenedicarboxylate (DMAD). Reaction of an equilibrium 87:13 mixture of **2b**:**3b** with DMAD (5 equiv)[13] in CD_2Cl_2 at 40 °C was followed by ^1H NMR spectroscopy over 10 days. Both isobenzofuryl carbene complex **3b** and alkyne complex **2b** disappeared and DMAD adduct **5b** formed in 68% NMR yield. Recrystallization gave **5b** in 48% yield as a red, crystalline solid (Scheme 9). DMAD adduct **4b** was characterized by ^1H and ^{13}C NMR spectroscopy and by HRMS. The ^{13}C NMR showed a

(9) Although isobenzofurans are highly reactive and somewhat unstable, they have been shown to be useful synthetic intermediates. (a) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1999**, *73*, 1. (b) Wege, D. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press Inc.: Greenwich, 1998; Vol. 4, p 1.

(10) The complexed alkyne of $C_5Me_5(CO)_2Re(H_3CC{\equiv}CCH_2OH)$ underwent slow rotation at room temperature and showed diastereotopic $Re(CO)_2$ and CH_2; dynamic NMR measurements gave $\Delta G^{\ddagger}_{rot} = 16.9$ kcal mol^{-1}. The related complex $C_5Me_5(CO)_2Re(HC{\equiv}CCH_2OH)$ underwent fast rotation at room temperature, showing equivalent CH_2; dynamic NMR measurements gave $\Delta G^{\ddagger}_{rot} = 12.2$ kcal mol^{-1}. Casey, C. P.; Selmeczy, A. D.; Nash, J. R.; Yi, C. S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1996**, *118*, 6698.

(11) Furan carbons adjacent to oxygen had chemical shifts between 166 and 172 ppm in (2-(5-phenyl)furyl)carbene complexes of Cr and W.[6]

(12) The effect of aryl substituents on the ^{13}C NMR chemical shifts of M=C in metal carbene complexes is small and nonsystematic.[1a,b] (a) Kraft, S. Ph.D. Thesis, University of Wisconsin−Madison, 2001; pp 153−164. (b) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413. (c) Bernasconi, C. F.; García-Río, L. *J. Am. Chem. Soc.* **2000**, *122*, 3821.

(13) Cleaner reactions were seen when a large excess of DMAD was employed. The large excess favors reaction of **3b** with DMAD as a dienophile over reaction of **3b** with the product **4b** acting as a dienophile.

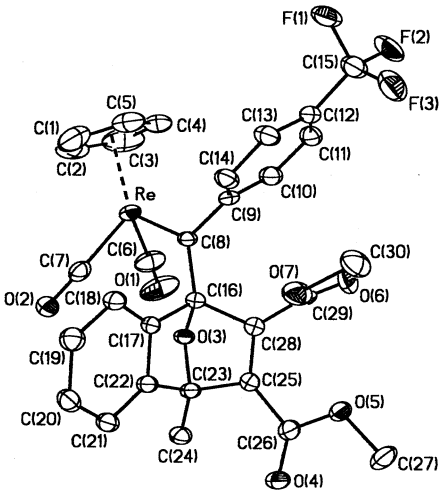


Figure 1. X-ray crystal structure of **4c**. Selected bond lengths (Å) and angles (deg): Re═C(8), 1.950(5); Re−C(8)−C(16), 125.9(3); Re−C(8)−C(9), 120.3(3); C(9)−C(8)−C(16), 113.7(3); Re−C(8)−C(16)−C(28), 155.7(3).

high-frequency carbene carbon resonance at δ 288.6, consistent with the structure of **4b**. IR spectroscopy showed two strong peaks for the metal carbonyls at 1986 and 1910 cm^{-1}.

The CF_3-substituted DMAD adduct **4c** was prepared by reaction of an equilibrium 57:43 mixture of **2c**:**3c** with DMAD (10 equiv)[13] in CD_2Cl_2 (Scheme 9). After 2 days at 38 °C, both starting materials **2c** and **3c** were consumed and **4c** was produced in 94% NMR yield. Recrystallization gave an 81% yield of **4c** as red crystals. Spectral characterization of **4c** included a ^{13}C NMR resonance for the carbene carbon at δ 284.3 and strong IR stretches for the metal carbonyls at 1990 and 1913 cm^{-1}. The X-ray crystal structure of **4c** (Figure 1, Table 1) confirmed the spectral assignments.[14] The structure contained one CH_2Cl_2 molecule per unit cell and showed some disorder about one of the carboxyl groups.

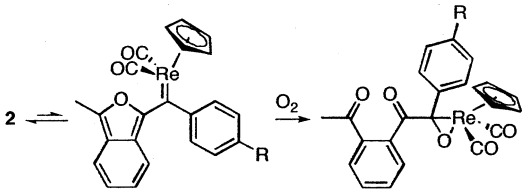
The isolation of complexes **4b** and **4c** offers strong support for the structures of isobenzofuryl carbene complexes **3b** and **3c**. Isolation and handling of carbene complex **4** in air demonstrates the high stability of Re carbene complexes toward oxidation.

Reaction of Rhenium Isobenzofuryl Carbene Complexes with O_2. When an equilibrium mixture of **2a** and **3a** in CD_2Cl_2 was exposed to air, isobenzofuryl carbene complex **3a** disappeared over several hours, followed by much slower disappearance of alkyne complex **2a** over 100 h (Scheme 10). This indicated that Re isobenzofurylcarbene complex **3a** was reacting directly with oxygen and is consistent with depletion of Re alkyne complex **2a** by slow equilibration with **3a** followed by oxidation of **3a**. ^1H NMR spectroscopy showed the formation of a single major product **5a** in 65% yield

Table 1. X-ray Crystal Data for 4c and 5a

	DMAD adduct **4c**	ketone complex **5a**
empirical formula	$C_{31}H_{24}Cl_2F_3O_7Re$	$C_{23}H_{17}O_5Re$
fw	823.61	559.59
temperature	100(2) K	100(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	monoclinic
space group	P	*C*2/*c*
unit cell dimens	a = 10.4367(6) Å b = 11.0323(6) Å c = 14.0659(8) Å α= 69.8650(10)° β= 80.7060(10)° γ= 79.2990(10)°	a = 14.6965(17) Å b = 11.6450(13) Å c = 11.9051(14) Å α= 90° β= 107.666(2)° γ= 90°
volume	1485.75(14) $Å^3$	1941.4(4) $Å^3$
Z	2	4
density (calcd)	1.841 Mg/m^3	1.914 Mg/m^3
abs coeff	4.336 mm^{-1}	6.292 mm^{-1}
F(000)	806	1080
crystal size	0.35 × 0.35 × 0.20 mm^3	0.43 × 0.19 × 0.10 mm^3
θ range for data collection	2.00 to 26.37°	2.27 to 28.30°
index ranges	$-12 \le h \le 13$, $-12 \le k \le 13$, $0 \le l \le 17$	$-19 \le h \le 19$, $-15 \le k \le 15$, $-15 \le l \le 15$
no. of reflns collected	12 311	8621
no. of indep reflns	5992 [R(int) = 0.0498]	2390 [R(int) = 0.0380]
completeness to θ = 26.37°	98.70%	98.70%
abs corr	multiscan with SADABS	multiscan with SADABS
max. and min. transmn	0.4776 and 0.3122	0.5719 and 0.1728
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/ restraints/ params	5992/31/398	2390/0/185
goodness-of-fit on F^2	1.037	1.207
final R indices [$I > 2\sigma(I)$]	R1 = 0.0302, wR2 = 0.0722	R1 = 0.0339, wR2 = 0.0931
R indices (all data)	R1 = 0.0335, wR2 = 0.0738	R1 = 0.0343, wR2 = 0.0933
largest diff peak and hole	2.070 and −1.858 e $Å^{-3}$	2.242 and −1.211 e $Å^{-3}$

Scheme 10



3

5a: R = H 65%
5b: R = OCH_3 66%
5c: R = CF_3 67%

determined by NMR integration using solvent as an internal standard.

Preparative TLC gave **5a** as an air-stable, yellow solid, which was characterized spectroscopically and by X-ray crystallography. HRMS showed that the conversion of **3a** to **5a** involved the addition of two oxygens. ^1H NMR spectroscopy provided evidence for the formation of a methyl ketone (singlet at δ 2.74), the destruction of the isobenzofuran system (disappearance of lower frequency resonances δ 7.08−6.80), and the generation of a normal aromatic system (appearance of higher frequency aromatic resonances between δ 7.42 and

(14) Re−C single bonds in the crystal structure of the metallacycle $Cp(CO)_2ReCH_2CH_2CH_2CH_2$ had lengths of 2.246(9) and 2.255(8) Å.[14a] The Re−C single bonds in the complex *cis*-$Cp(CO)_2Re(CH_2CH_3)_2$ had lengths of 2.262(10) and 2.263(10) Å.[14b] The Re═C double bond distance in the complex $Cp(CO)_2Re{=}C(Tol)(C{\equiv}CTol)$ was 2.004(5) Å.[1a,12a] Re═C double bond distances in the complexes $Cp(CO)_2Re{=}C(C_6H_4$-*p*-$SO_2CF_3)C{\equiv}CC_6H_4$-*p*-$CH_3$,[1b] ($\eta^5$-indenyl)$(CO)_2Re{=}C(C_6H_4$-*p*-$CF_3)C{\equiv}CC_6H_4$-*p*-$CH_3$,[1b] and $Cp^*(CO)_2Re{=}C(Ph)C{\equiv}CPh^2$ were 2.007(5), 1.996(4), and 2.004(5) Å, respectively. (a) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129. (b) Klahn, A. H.; Manzur, C.; Toro, A.; Moore, M. *J. Organomet. Chem.* **1996**, *516*, 51.

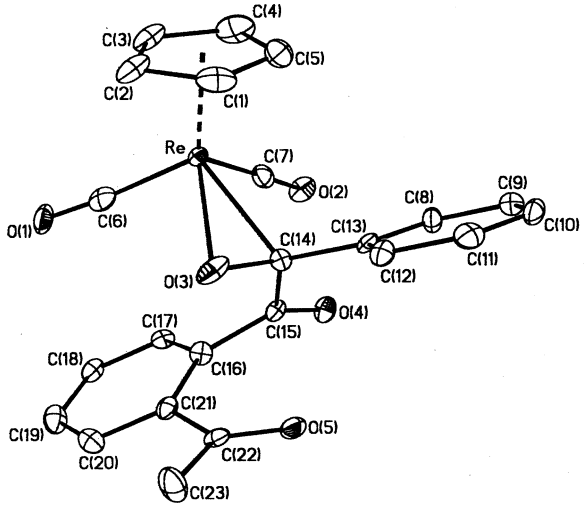


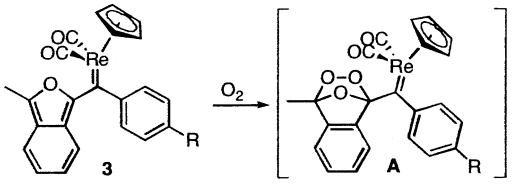
Figure 2. X-ray crystal structure of **5a**. Selected bond lengths (Å) and angles (deg): Re−O(3), 2.161(10); Re−C(14), 2.205(3); O(3)−C(14), 1.400(12); O(4)═C(15), 1.215-(9); O(5)═C(22), 1.228 (10); Re−O(3)−C(14), 73.0(5); O(3)−Re−C(14), 37.4(3); O(3)−C(14)−Re, 69.6(4); O(3)−C(14)−C(13), 117.7(4); C(13)−C(14)−C(15), 118.1; O(3)−C(14)−C(15)−O(4), 178.1(7); O(4)−C(15)−C(16)−C(17), 51.8(5); C(16)−C(21)−C(22)−O(5), 19.4(5).

7.68). ^{13}C NMR spectroscopy of **5a** showed two metal carbonyl resonances and two organic carbonyl resonances (δ 205.3, 201.1, 199.1, 197.8). IR spectroscopy showed two very strong bands at 1999 and 1925 cm^{-1} for the metal carbonyls and two weaker bands at 1692 and 1668 cm^{-1} for the organic carbonyls.

While spectroscopic data were consistent with the structure depicted for **5a**, X-ray crystallography was required to establish its structure as an η^2-ketone complex (π-bonded to metal) (Figure 2, Table 1). η^1-Ketone complexes (lone pair σ-bonded to metal) are more common than η^2-ketone complexes (π-bonded to metal).[15] η^2-Complexation is usually seen for aldehydes,[15,16] but has only occasionally been seen for ketones. For example, a Re-η^2-ketone complex was seen for a ketone having electron-withdrawing groups (Cl, F) α to the carbonyl.[15] The η^2-ketone coordination seen in **5a** may be favored by the electron-withdrawing nature of its aroyl substituent. There are two resonance structures for η^2-ketone complexes: π-bond coordination to the metal and a metallaoxirane formulation. The ^{13}C NMR chemical shift of complexed carbonyl (δ 78.4) of **5a** suggests that the metallaoxirane formulation is the major resonance contributor.

Unusual spectral features of **5a** are readily understood in light of its η^2-ketone structure. The unusual ^{13}C NMR resonance at δ 78.4 is assigned to the η^2-complexed carbonyl of **5a**. The ^{1}H NMR resonance at δ 7.81, corresponding to the ortho protons of the phenyl group, was very broad. Upon cooling to −62 °C, this ortho resonance decoalesced to give peaks at δ 8.42 and

Scheme 11



7.19. The appearance of two resonances is due to slow rotation of the phenyl group about C(13)−C(14) (Figure 2). Phenyl rotation is apparently hindered by steric interactions with the Cp group on Re and by the electronic requirement of breaking conjugation with the coordinated ketone carbonyl. A rotation barrier of $\Delta G^{\ddagger}$ of 12.9 ± 0.5 kcal mol^{-1} was estimated from the low-temperature peak separations and the coalescence temperature of 20 °C. Slow rotation of the phenyl group also gave rise to a very broad resonance at δ 127 for the ortho carbons in the ^{13}C NMR spectrum.

The related η^2-ketone complexes **5b** (66% yield) and **5c** (67% yield) were prepared in a similar fashion by air oxidation of equilibrating mixtures of **2** and **3**. The ^{1}H NMR spectra of **5b** and **5c** were similar to that of **5a**; very broad ortho hydrogen resonances were seen at δ 7.69 for **5b** and 7.90 for **5c**, indicating hindered aryl rotation. In the ^{13}C NMR spectra, resonances at δ 78.9 for **5b** and 76.2 for **5c** were observed for the η^2-ketone carbonyl carbons. Ketone complexes **5b** and **5c** each showed two strong IR absorbances for the metal carbonyls (**5b**: 1994, 1922 cm^{-1}; **5c**: 2001, 1929 cm^{-1}).

^{17}O-Labeling Studies of Formation of η^2-Ketone Complexes. The more rapid disappearance of the isobenzofuryl carbene complex **3** from the equilibrating mixture of **3** and alkyne complex **2** requires that **3** be the compound that reacts with oxygen. Since M═C bonds are often subject to oxidation, we considered mechanisms for oxidation of **3** that involved initial attack of O_2 at the metal carbene unit. This would place one of the newly incorporated oxygens on the η^2-ketone carbonyl (the former carbene carbon of **3**). Since isobenzofurans are easily oxidized to endoperoxides,[17] we also considered the possibility that oxidation of **3** initially produced endoperoxide **A** (Scheme 11). The conversion of isobenzofuran endoperoxides to 1,2-dialkanoylbenzenes has been observed, though it is not clear how an oxygen atom is lost from the endoperoxide.[17] Furan endoperoxides and isobenzofuran endoperoxides are oxidizing agents and have been observed to transfer oxygen atoms to alkenes to form epoxides and to diphenylsulfides to form sulfoxides.[17b,18] Consequently, there are many possible pathways from **A** to the observed η^2-ketone complex **5**, and it is possible to write mechanisms that place the unique furyl oxygen on any of the three sites in **5**. To help distinguish between these possibilities, we studied the reaction of an equilibrating mixture of **2** and **3** with ^{17}O-labeled dioxygen.

The two ketone carbonyls of **5** were expected to be seen in the δ 500−600 ppm range based on comparisons

(15) (a) Klein, D. P.; Dalton, D. M.; Méndez, N. Q.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7. (b) Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446.

(16) (a) Schuster, D. M.; White, P. S.; Templeton, J. L. *Organometallics* **2000**, *19*, 1540. (b) Garner, C. M.; Méndez, N. Q.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (c) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

(17) Dioxygen addition to isobenzofurans, in both the presence and absence of light, has been demonstrated to produce endoperoxides. (a) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *26*, 135. (b) Saito, I.; Nakata, A.; Matsuura, T. *Tetrahedron Lett.* **1981**, *22*, 1697. (c) Johansson, E.; Skramstad, J. *J. Org. Chem.* **1981**, *46*, 3752. (d) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 3849.

(18) Adam, W.; Rodriguez, A. *J. Am. Chem. Soc.* **1980**, *102*, 404.

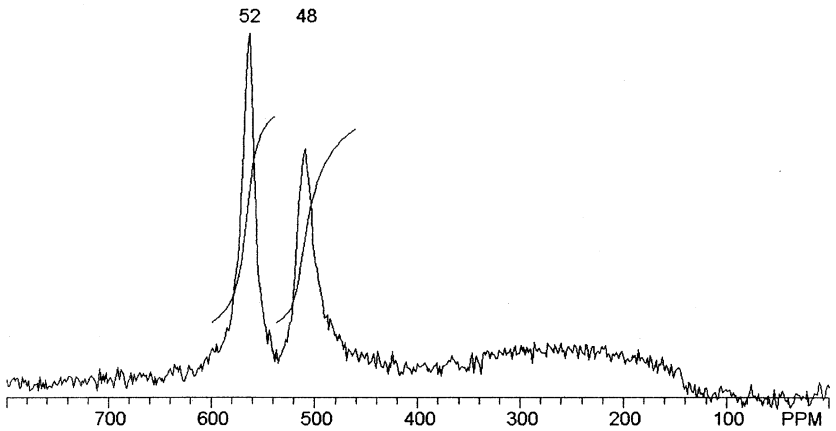


Figure 3. ^{17}O NMR spectrum of **5a** produced from reaction of 10% ^{17}O-labeled O_2 with **3a**.

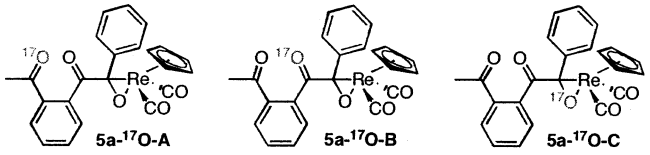


Figure 4. Three singly ^{17}O-labeled isotopomers of **5a**.

with acetophenone (δ 542.5),[19] acetone (δ 569),[20] and 1,2-diphenyl-1,2-ethanedione (δ 541).[21] A natural abundance ^{17}O NMR spectrum of 1,2-diacetylbenzene, which closely models the chemical environment of the methyl ketone moiety of **5a**, showed a resonance at δ 563.5. Since no analogous η^2-ketone complexes were known, we needed to make an appropriate model compound to assign the η^2-complexed carbonyl. The η^2-ketone complex, $Cp(CO)_2Re(\eta^2$-benzil) (**6**), was prepared in 9.2% yield by reaction of benzil ($C_6H_5(C{=}O)(C{=}O)C_6H_5$) with $Cp(CO)_2Re(THF)$. A ^{13}C NMR resonance at δ 78.1 established that **6** was an η^2-ketone complex. The natural abundance ^{17}O NMR spectrum showed a broad resonance at δ 144.3 assigned to the oxygen of the η^2-ketone unit in addition to a broad resonance at δ 523.0 for the organic carbonyl and sharp resonances at δ 379.8 and 377.2 for the diastereotopic $Re(CO)_2$ unit.[22]

Reaction of 10% ^{17}O-enriched dioxygen with an equilibrium mixture of **2a**:**3a** gave ^{17}O-labeled **5a**,which was isolated by preparative TLC. The ^{17}O NMR spectrum of labeled **5a** showed a 52:48 ratio of two resonances at δ 564.6 and 510.4 corresponding to two of the three ^{17}O isotopomers (Figure 3).[23] No ^{17}O NMR resonance was seen in the δ 140 range expected for an η^2-ketone complex as in **5a-^{17}O-C** (Figure 4). On the basis of chemical shift comparisons, the δ 564.6 resonance was assigned to the methyl ketone in **5a-^{17}O-A** and the δ 510.4 resonance was assigned to the second organic carbonyl in **5a-^{17}O-B** (Figure 4).

In an analogous experiment, reaction of 10% ^{17}O-enriched dioxygen with an equilibrium mixture of **2c**:**3c** gave ^{17}O-labeled **5c**, which was isolated by preparative TLC. The ^{17}O NMR spectrum of labeled **5c** showed a 51:49 ratio of two resonances at δ 564.6 and 509.1, corresponding to two of the three ^{17}O isotopomers. No resonance was seen for the η^2-ketone unit of **5c-^{17}O-C**.

Since two new oxygens are introduced in the conversion of **3** to **5**, selective routes to **5** will put equal amounts of ^{17}O label into two sites and leave one site unlabeled. The nearly 50:50 mixture of **5-^{17}O-A**:**5-^{17}O-B** observed is consistent with a single mechanistic pathway. The absence of any **5-^{17}O-C** isotopomer requires that this pathway involve movement of the isobenzofuran oxygen of **3** to the η^2-ketone unit of **5**. In this process, both C−O bonds of the furan are severed, the furan oxygen migrates to the former carbene carbon, and dioxygen supplies the carbonyl oxygens of the noncomplexed ketones. Clearly, profound rearrangements are involved.

Discussion

The interesting interconversions of Re alkyne complexes **2a**−**c** and Re isobenzofuryl carbene complexes **3a**−**c**[24] can be viewed in two ways. They can be viewed as proceeding by a nucleophilic attack of the ketone carbonyl on the alkyne complexed to rhenium (Scheme 8). However, Re alkyne complexes are generally not susceptible to nucleophilic attack. Another view involves an initial [1.5,1] shift of Re to one carbon of the alkyne in **2**, which would lead to "free carbene" character at the other alkyne carbon (Scheme 8). The "free carbene" could then be trapped through cyclization to give isobenzofuran **3**. It is known that 4-oxabutadienyl carbenes undergo 6π electrocyclizations to produce furan derivatives.[5] Unfortunately, we do not yet have a way to distinguish between a nucleophilic attack pathway and a "free carbene" pathway. We are trying to devise other traps to test for carbene reactivity at one carbon of a metal-alkyne complex.

Earlier, 2-furylcarbene complexes of Cr and W were generated by reacting $M(CO)_5(THF)$ with *cis*-2-penten-4-yn-1-ones (Scheme 4).[6,8] It was suggested that the reaction proceeded by alkyne coordination followed by ring-closing rearrangement. However, the metal alkyne complex was never detected, presumably because ring-closing rearrangement was so rapid.

(19) Chimichi, S.; Dell'Erba, C.; Gruttadauria, M.; Noto, R.; Novi, M.; Petrillo, G.; Sancassan, F.; Spinelli, D. *J. Chem. Soc., Perkin. Trans. 2* **1995**, 1021.

(20) Delseth, C.; Kintzinger, J. P. *Helv. Chim. Acta* **1976**, *59*, 466.

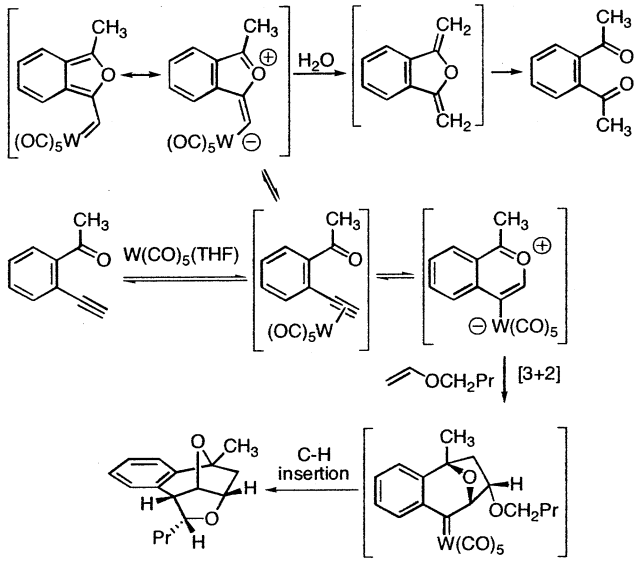
(21) Cerioni, G.; Plumitallo, A.; Frey, J.; Rappoport, Z. *Magn. Reson. Chem.* **1995**, *33*, 874.

(22) Kintzinger, J. P. *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; pp 79−104.

(23) On the basis of the extent of baseline rolling and phasing error in this ^{17}O NMR spectrum, integrations are estimated to be accurate to within ~10%.

(24) **3a**−**c** are the first spectrally characterized isobenzofuryl carbene complexes.

Scheme 12



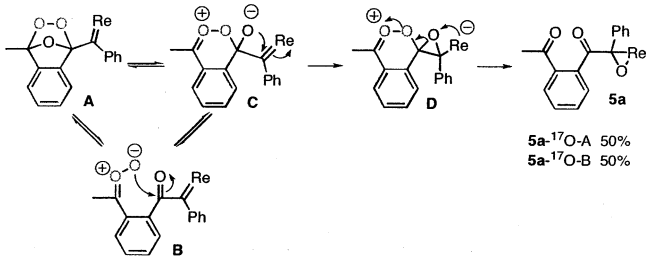
In the 2′-alkynylacetophenone systems reported here, the diminished aromatic character of the isobenzofuran unit relative to a furan greatly changes the relative energies of the starting alkyne complex and the cyclized products. This made it possible to observe both alkyne complexes **2** and isobenzofuryl carbene complexes **3** in equilibrium. There is presumably also significant transition state destabilization leading to the isobenzofuryl carbene complexes, which greatly slows the rate of conversion of **2** to **3** and makes isolation of pure alkyne complexes possible.

The destabilizing effect of the isobenzofuran was so great that the alkyne complexes **2** were significantly more stable than the isomeric isobenzofuryl carbene complexes **3**. The small percentages of the carbene complexes **3** made their identification difficult and their isolation virtually impossible. In an effort to stabilize the isobenzofuryl carbene complex, an electron-donating methoxy substituent was added to the aryl ring. It was expected that electron donation to the electron-deficient carbene carbon of **3b** would selectively stabilize it relative to alkyne complex **2b**. Surprisingly, the electron-donating methoxy substituent had the opposite effect, and an even less favorable equilibrium ratio of **2b**:**3b** was obtained than in the phenyl derivative. Use of a strongly electron-withdrawing trifluoromethyl group gave more of the carbene complex **3c** in equilibrium with alkyne complex **2c**. We do not understand these electronic substituent effects on the relative stability of **2** and **3**.

Solvent effects on the equilibrium between **2** and **3** were small, but systematic. The equilibrium was shifted more toward the Re alkyne complexes **2** in solvents of higher dielectric constant. The alkyne complexes possess a polar ketone group that can be selectively stabilized by the polar solvents.

It is interesting that five-membered-ring (isobenzofuran) formation was exclusively observed in our study. This contrasts with recent work by Iwasawa, which showed the possibility of six-membered-ring formation. Iwasawa reported reactions of *o*-ethynylphenyl ketones with $W(CO)_5$(THF) that appear to proceed via tungsten alkyne complexes that lead to six-membered-ring formation by nucleophilic attack of the carbonyl on the remote carbon of the complexed alkyne (Scheme 12).[7,25] The resulting carbonyl ylide intermediates were suggested to be trapped by electron-rich alkenes (*n*-butyl vinyl ether) in a [3+2] cycloaddition; subsequent insertion of the resulting tungsten carbene into a C−H bond gave rise to the observed polycyclic products.[7,25] Iwasawa also reported reactions of *o*-ethynylphenyl ketones with $W(CO)_5$(THF) in the presence of water that appear to proceed via tungsten alkyne complexes that lead to five-membered-ring intermediates and products.[7,25]

Scheme 13



In an attempt to trap a possible six-membered-ring carbonyl ylide intermediate in our system, we monitored a solution containing an equilibrium mixture of **2a** and **3a** and excess *n*-butyl vinyl ether over 3 weeks, but saw no reaction. The origin of the preference for exclusive five-membered-ring formation over six-membered-ring formation in our system is not understood but may be dependent on alkyne substitution.

To more fully characterize Re isobenzofuryl carbene complexes **3**, it was necessary to establish their structures through trapping experiments. Treatment of **3** with the electron-deficient alkyne DMAD gave Re carbene complexes **4** through Diels−Alder cycloadditions. This confirmed the structure of **3** and demonstrated the stability of the Re carbene moiety through the isolation of **4** in air.

The isobenzofuryl carbene complex **3** was trapped with dioxygen, which gave ketone complex **5**. ^{17}O-labeling studies showed that there was a single pathway for oxidation that requires migration of the isobenzofuran oxygen to the η^2-ketone oxygen in **5** and cleavage of the two C−O bonds of the isobenzofuran. We propose that this pathway starts with endoperoxide **A**. We suggest that this pathway proceeds by opening of the endoperoxide to the carbonyl oxide−ketone intermediate **B** (this is the microscopic reverse of a dipolar [3+2] cycloaddition) (Scheme 13). Attack of the nucleophilic oxygen of the carbonyl oxide on the ketone unit would produce zwitterion **C**, which might also be formed directly from **A** by opening of the five-membered ring. Attack of the anionic oxygen of **C** on the electrophilic carbene carbon would produce epoxide **D,** which could then fragment to **5** (Scheme 13).

Experimental Section

2′-(Phenylethynyl)acetophenone (1a).[26] Et_3N (2.70 mL, 19.4 mmol), 2′-iodoacetophenone (2.50 g, 10.2 mmol), and phenylacetylene (1.41 mL, 12.8 mmol) were

(25) Iwasawa, N.; Kusama, H.; Maeyama, K. *J. Synth. Org. Chem., Jpn.* **2002**, 1036.
(26) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem., Eur. J.* **1997**, *3*, 807.

added to a mixture of CuI (97 mg, 0.51 mmol) and $Pd(PPh_3)_4$ (236 mg, 0.204 mmol) in toluene (75 mL). Upon stirring for 24 h at 40 °C, the yellow reaction mixture turned black. Saturated aqueous NH_4Cl (70 mL) was added at room temperature, and the mixture was extracted with EtOAc (3 × 40 mL). The combined organic extract was dried ($MgSO_4$), filtered, and concentrated on a rotary evaporator. Flash column chromatography (silica gel, 100:6 pentane:ether) gave **1** as an orange oil (1.89 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (ddd, J = 7.7, 1.5, 0.5 Hz, 1H), 7.63 (ddd, J = 7.7, 1.5, 0.5 Hz, 1H), 7.58−7.52 (m, 2H), 7.47 (td, J = 7.5, 1.5 Hz, 1H), 7.40 (td, J = 7.7, 1.5 Hz, 1H), 7.39−7.35 (m, 3H), 2.80 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 200.2 (C═O), 140.6, 133.7, 131.3 (2C), 131.1, 128.6, 128.5, 128.3 (2C), 128.1, 122.7, 121.5, 94.8 (*C*≡C), 88.3 (C≡*C*), 29.8 (Me).

2′-((*p*-Methoxyphenyl)ethynyl)acetophenone (1b) was prepared from 1-ethynyl-4-methoxy benzene (1.66 mL, 12.8 mmol) by a procedure similar to that used for **1a**. Flash column chromatography (silica gel, 10:1 pentane/ether) gave **1b** (2.24 g, 88%) as an orange crystalline solid, mp 51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, J = 7.7, 1.4 Hz, 1H), 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 2.79 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.4 (C═O), 160.1, 140.6, 133.8, 133.1 (2C), 131.4, 128.8, 128.0, 122.2, 115.1, 114.2 (2C), 95.4 (*C*≡C), 87.5 (C≡*C*), 55.4 (OMe), 30.1 (Me). HRMS (EI): calcd for $C_{17}H_{14}O_2$ 250.0994, found 250.0986.

2′-((*p*-(α,α,α-Trifluorotolyl)ethynyl)acetophenone (1c) was prepared from 4-ethynyl-α,α,α-trifluorotoluene (1.56 mL, 9.6 mmol) by a procedure similar to that used for **1a** and isolated as a brown oil (2.71 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (ddd, J = 7.5, 1.5, 0.6 Hz, 1H), 7.69−7.60 (m, 5H), 7.51 (td, J = 7.5, 1.8 Hz, 1H), 7.44 (td, J = 7.5, 1.5 Hz, 1H), 2.76 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.8 (C═O), 140.9, 134.3, 132.0 (2C), 131.6, 130. 5 (q, J_{CF} = 33 Hz), 129.1, 129.0, 127.0 (q, J_{CF} = 1.5 Hz), 125.5 (q, J_{CF} = 3.8 Hz, 2C), 124.1 (q, J_{CF} = 272 Hz, CF_3), 121.1, 93.2(*C*≡C), 91.0(C≡*C*), 29.8 (Me). HRMS (ESI): calcd for $C_{17}H_{11}F_3ONa$ (M + Na^+) 311.0660, found 311.0647.

Cp(CO)$_2$Re[η^2-(2′-(phenylethynyl)acetophenone)] (2a). A solution of $CpRe(CO)_3$ (0.600 g, 1.79 mmol) in dry degassed THF (140 mL) was photolyzed with a Hanovia medium-pressure mercury lamp for 30 min at 0 °C with continuous N_2 purging. The disappearance of $CpRe(CO)_3$ [2022 (m) and 1926 cm^{-1}(s)] and the appearance of $CpRe(CO)_2(THF)$ [1912 (s) and 1839 cm^{-1} (s)] was monitored by IR spectroscopy. **1a** (1.89 g, 8.57 mmol) was added, and the solution was concentrated to 15 mL on a rotary evaporator. The brown solution was stirred under N_2 at 0 °C for 2 h and at room temperature for an additional 3 h. Preparative TLC (silica gel, 2:1 pentane/ether) gave **2a** (79.8 mg, 8.5%, R_f = 0.38) as an air-stable, brown solid and 63% recovered **1a** (R_f = 0.62). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.61 (ddd, J = 7.5, 1.5, 0.5 Hz, 1H), 7.56−7.52 (m, 3H), 7.51 (ddd, J = 7.5, 1.8, 0.5 Hz, 1H), 7.40−7.35 (m, 3H), 7.30 (tt, J = 7.5, 1.3 Hz, 1H), 5.60 (s, Cp), 2.31 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 205.5 (v br, CO), 202.2 (C═O), 140.4, 133.6, 132.1, 131.8 (2C), 131.7, 131.5, 128.98, 128.96 (2C), 128.5, 127.4, 89.2 (Cp), 87.0 (*C*≡C), 79.9(C≡*C*), 29.3 (Me). HRMS (EI): calcd for $C_{23}H_{17}O_3{}^{185}Re$ (M^+) 526.0707, found 526.0706.

Cp(CO)$_2$Re[η^2-(2′-((*p*-methoxyphenyl)ethynyl)acetophenone)] (2b) was prepared from **1b** (1.8 g, 7.2 mmol) using the procedure described for **2a**. Preparative TLC (silica gel, 1:1 pentane/ether) gave **2b** (60 mg, 6.0%, R_f = 0.40) and >85% of recovered **1b** (R_f = 0.71). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 7.8 Hz, 1H), 7.54−7.46 (m, 4H), 7.34 (ddd, J = 7.5, 4.8, 3.9 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 5.57 (s, Cp), 3.84 (s, OMe), 2.28 (s, Me). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ 204.97 (CO), 204.95(CO), 203.2 (C═O), 159.9, 140.7, 133.0 (2C), 131.4, 131.4, 128.5, 127.0, 124.0, 114.2 (2C), 112.8, 91.0 (*C*≡C), 88.6 (Cp), 87.7 (C≡*C*), 55.6 (OMe), 29.2 (Me). HRMS (EI): calcd for $C_{24}H_{19}O_4{}^{187}Re$ (M^+) 558.0841, found 558.0839.

Cp(CO)$_2$Re[η^2-(2′-((*p*-(α,α,α-trifluorotolyl)ethynyl)acetophenone)] (2c) was prepared from **1c** (1.10 g, 3.8 mmol) using the procedure described for **2a**. Preparative TLC (silica gel, 3:2 pentane/ether) gave **2c** (44 mg, 4.1%, R_f = 0.50) and 78% of recovered **1c** (R_f = 0.73). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.67, (ddd, J = 7.8, 1.5, 0.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.56 (ddd, J = 8.0, 7.5, 1.5 Hz, 1H), 7.49 (ddd, J = 7.8, 1.5, 0.5 Hz, 1H), 7.41 (ddd, J = 7.8, 7.2, 1.5 Hz, 1H), 5.61 (s, Cp), 2.36 (s, Me). ^{1}H NMR (300 MHz, C_6D_6): δ 7.51 (d, J = 8.4 Hz, 2H), 7.43 (ddd, J = 7.5, 1.5, 0.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.27 (ddd, J = 7.8, 1.5, 0.6 Hz, 1H), 7.12 (dt, J = 7.8, 1.5 Hz, 1H), 6.93 (td, J = 7.8, 1.2 Hz, 1H), 4.92 (s, Cp), 2.08 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 4 °C): δ 205.5 (CO), 204.8 (CO), 201.7 (C═O), 139.6, 136.0 (q, J_{CF} = 1.5 Hz), 133.3, 131.9, 131.6 (2C), 131.1, 129.2 (q, J_{CF} = 33 Hz), 129.2, 127.7, 125.7 (q, J_{CF} = 3.8 Hz, 2C), 89.3 (Cp), 85.18 (*C*≡C), 85.16 (C≡*C*), 29.2 (Me), CF_3 resonance not observed. HRMS (EI): calcd for $C_{22}H_{16}F_3O_1{}^{185}Re$ ($M - 2CO$)$^+$ 538.0683, found 538.0692. Molecular ion peak was too small to be observed.

Cp(CO)$_2$Re═C(C_6H_5)(C_9H_7O) (3a). A solution of **2a** in CD_2Cl_2, degassed by three freeze−pump−thaw cycles, was heated at 38 °C for 5 days in a resealable NMR tube to give a 76:24 equilibrium mixture of **2a**:**3a** (K_{eq} = 0.32). In $CDCl_3$, a 67:33 equilibrium mixture of **2a**:**3a** (K_{eq} = 0.50) was obtained; in toluene-d_8, a 57:43 equilibrium mixture of **2a**:**3a** (K_{eq} = 0.75) was obtained. ^{1}H NMR (500 MHz, CD_2Cl_2) of **3a**: δ 7.51 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.22 (tt, J = 7.5, 1.5 Hz, 1H), 7.08 (ddd, J = 9.0, 6.5, 1.0 Hz, 1H), 6.90 (m, 2H), 6.80 (ddd, J = 8.5, 6.5, 0.5 Hz, 1H), 5.28 (s, Cp), 2.22 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) of **3a**: δ 245.0 (Re═C), 206.2 (CO), 162.7, 161.3, 159.1, 129.6, 128.3, 127.8 (2C), 125.8, 125.2, 124.2, 123.4, 122.3 (2C), 120.0, 91.5 (Cp), 15.063 (Me).

Cp(CO)$_2$Re═C(C_6H_4-*p*-OMe)(C_9H_7O) (3b). A solution of **2b** in CD_2Cl_2, degassed by three freeze−pump−thaw cycles, was monitored by NMR spectroscopy at room temperature for 3 days (~20 × $t_{1/2}$). An 87:13 equilibrium mixture of **2b**:**3b** (K_{eq} = 0.15) was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.26 (s, Cp), 3.86 (s, OMe), 2.20 (s, Me). Aromatic and vinyl resonances were obscured by **2b**.

Cp(CO)$_2$Re═C(C_6H_4-*p*-CF_3)(C_9H_7O) (3c). A solution of **2c** in CD_2Cl_2, degassed by three freeze−pump−thaw

cycles, was heated at 38 °C for 3 days in a resealable NMR tube to give a 57:43 equilibrium mixture of **2c**:**3c** ($K_{eq} = 0.74$). In benzene-d_6, a 38:62 equilibrium mixture of **2c**:**3c** ($K_{eq} = 1.63$) was obtained. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.62 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.13 (ddd, $J = 9.0, 6.6, 0.9$ Hz, 1H), 7.08−7.02 (m, 2H), 6.83 (ddd, $J = 8.7, 6.6, 0.3$ Hz, 1H), 5.28 (s, Cp), 2.20 (s, Me). ^{1}H NMR (300 MHz, C_6D_6): δ 7.31 (d, $J = 8.1$ Hz, 2H, Ph), 6.84 (dt, $J = 8.4, 0.9$ Hz, 1H), 6.78 (ddd, $J = 8.7, 6.6, 0.9$ Hz, 1H), 6.67 (d, $J = 7.8$ Hz, 2H, Ph), 6.36 (ddd, $J = 8.7, 6.6, 0.6$ Hz, 1H), 5.59 (dt, $J = 9.0, 0.9$ Hz, 1H), 4.76 (s, Cp), 1.56 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 240.9 (Re=C), 205.9 (CO), 164.9, 162.2, 160.0, 130.2, 128.3, 125.5, 125.1 (q, $J_{CF} = 3.5$ Hz, 2C), 124.5, 123.1, 122.7 (2C), 120.3, 91.5 (Cp), 15.1 (Me). The resonances for CF_3 and CCF_3 were not observed.

DMAD Adduct Cp(CO)$_2$Re=C(C$_6$H$_4$-*p*-OMe)(C$_{15}$H$_{13}$O$_5$) (4b). Dimethyl acetylenedicarboxylate (DMAD) (18 μL, 0.15 mmol) was added to a CD_2Cl_2 solution of an equilibrium mixture of **2b**:**3b** (17.0 mg, 0.030 mmol) in a resealable NMR tube. After 10 days at 40 °C, a 68% yield of **4b** was observed by NMR spectroscopy. Evaporation of CD_2Cl_2 and most of the DMAD under vacuum (3.0×10^{-2} mm), followed by crystallization of the residue from CH_2Cl_2/pentane, gave **4b** (10 mg, 48%) as an air-stable red crystalline solid. IR (THF): 1986 (C≡O), 1910 (C≡O) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.24 (ddd, $J = 7.2, 1.2, 0.6$ Hz, 1H), 7.02 (td, $J = 7.4, 0.9$ Hz, 1H), 6.97 (d, $J = 9.0$ Hz, 2H), 6.89 (td, $J = 7.5, 1.2$ Hz, 1H), 6.78 (d, $J = 9.0$ Hz, 2H), 6.70 (dt, $J = 7.2, 0.9$ Hz, 1H), 5.44 (s, Cp), 3.84 (s, OMe), 3.66 (s, OMe), 3.41 (s, OMe), 2.06 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 288.6 (Re=C), 204.1(CO), 204.0 (CO), 165.5 (CO_2), 163.5(CO_2), 158.8, 158.5, 155.3, 151.8, 149.9, 148.8, 125.8, 125.7, 123.8, 122.0 (2C), 119.6, 112.6, 112.2 (2C), 93.5 (Cp), 88.9, 55.8 (OMe), 52.5 (OMe), 52.3 (OMe), 14.7 (Me). HRMS (ESI): calcd for $C_{30}H_{25}O_8{}^{185}$ReNa (M + Na$^+$) 721.0971, found 721.0950.

DMAD Adduct Cp(CO)$_2$Re=C(C$_6$H$_4$-*p*-CF$_3$)(C$_{15}$H$_{13}$O$_5$) (4c). Dimethyl acetylenedicarboxylate (DMAD) (82 μL, 0.67 mmol) was added to a CD_2Cl_2 solution of an equilibrium mixture of **2c**:**3c** (40 mg, 0.067 mmol) in a resealable NMR tube. After 44 h at 38 °C, a 94% yield of **4c** was observed by NMR spectroscopy. Evaporation of CD_2Cl_2 and most of the DMAD under vacuum (3.0×10^{-2} mm), followed by crystallization of the residue from CH_2Cl_2/pentane, gave **4c** (40 mg, 81%) as an air-stable red crystalline solid. IR (THF): 1990 (C≡O), 1913 (C≡O) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.54 (d, $J = 8.1$ Hz, 2H), 7.25 (dt, $J = 7.2, 0.9$ Hz, 1H), 7.16 (d, $J = 8.1$ Hz, 2H), 7.02 (td, $J = 7.5, 0.9$ Hz, 1H), 6.88 (td, $J = 7.5, 1.2$ Hz, 1H), 6.60 (d, $J = 7.5$ Hz, 1H), 5.49 (s, Cp), 3.67 (s, OMe), 3.39 (s, OMe), 2.078 (s, Me). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 284.3 (Re=C), 203.5 (CO), 203.4 (CO), 169.0 (CO_2), 165.6 (CO_2), 163.6, 154.8, 151.7, 150.8, 149.0, 128.1 (q, $J_{CF} = 32$ Hz), 126.1, 126.0, 125.0 (q, $J_{CF} = 272$ Hz), 124.1 (q, $J_{CF} = 3.5$ Hz, 2C), 123.8, 120.3 (2C), 120.0, 93.9 (Cp), 89.4, 52.6 (OMe), 52.3 (OMe), 14.5(Me). The bridgehead carbon adjacent to the carbene carbon was not observed (possibly obscured by the broad resonance at δ 120.3). HRMS (ESI): calcd for $C_{30}H_{22}F_3O_7{}^{185}$ReNa (M + Na$^+$) 759.0745, found 759.0735.

Rhenium Ketone Complex Cp(CO)$_2$Re[η^2-O=C(C$_6$H$_5$)(C$_9$H$_7$O$_2$)] (5a). A CD_2Cl_2 solution of an equilibrium mixture of **2a**:**3a** was exposed to air and monitored by ^{1}H NMR spectroscopy. Isobenzofuran carbene complex **3a** disappeared over several hours and alkyne complex **2a** disappeared more slowly over 100 h to give a 65% yield of **5a**. Preparative TLC (silica gel, 2:1 pentane/ether) gave **5a** ($R_f = 0.06$) as an air-stable yellow solid. Recrystallization by slow diffusion of pentane into a solution of **5a** in pentane/CH_2Cl_2 gave fine yellow crystals of **5a**, suitable for X-ray crystal structure analysis. Alternatively, a mixture of **2a**:**3a** (20.5 mg) was exposed to O_2 (~4 atm) in CH_2Cl_2. After 2 days, preparative TLC gave **5a** (14.2 mg, 69%) as a yellow powder. IR (THF): 1999 (s, C≡O), 1925 (s, C≡O), 1692 (m, C=O), 1668 (m, C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (br, 2H), 7.68 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.59 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.50 (td, $J = 7.5, 1.2$ Hz, 1H), 7.42 (td, $J = 7.5, 1.4$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.18 (tt, $J = 7.4, 1.2$ Hz, 1H), 5.15 (s, Cp), 2.74 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 205.3 (ReCO), 201.1 (ReCO), 199.1 (C=O), 197.8 (C=O), 143.2, 139.7, 136.9, 131.9, 130.8, 129.8, 128.0 (2C), 127.0 (v br, 2C), 126.98, 126.6, 92.6 (Cp), 78.4 (CORe), 27.7 (Me). HRMS (ESI): calcd for $C_{23}H_{17}O_5{}^{185}$ReNa (M + Na$^+$) 581.0503, found 581.0492.

Rhenium Ketone Complex Cp(CO)$_2$Re[η^2-O=C(C$_6$H$_4$-*p*-OMe)(C$_9$H$_7$O$_2$)] (5b). A CD_2Cl_2 solution of an equilibrium mixture of **2b**:**3b** was exposed to air and monitored by ^{1}H NMR spectroscopy. **3b** disappeared over several hours and **2b** disappeared more slowly over 72 h to give a 66% yield of **5b**. Preparative TLC (silica gel, 1:1 pentane/ether) gave **5b** ($R_f = 0.10$) as a pale yellow oil. IR (THF): 1994 (C≡O), 1922 (C≡O) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.69 (br d, $J = 7.8$ Hz, 2H), 7.61 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.58 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.49 (td, $J = 7.5, 1.5$ Hz, 1H), 7.42 (td, $J = 7.5, 1.5$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 5.19 (s, Cp), 3.83 (s, OMe), 2.64 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 206.5 (ReCO), 201.3 (ReCO), 199.8 (C=O), 198.6 (C=O), 159.0, 140.1, 135.7, 132.1, 131.3, 131.0, 130.0, 129.1 (v br, 2C), 126.6, 113.6 (2C), 93.0 (Cp), 78.9 (CORe), 55.8 (OMe), 27.8 (Me). HRMS (ESI): calcd for $C_{24}H_{19}O_6{}^{187}$ReNa (M + Na$^+$) 613.0637, found 613.0663.

Rhenium Ketone Complex Cp(CO)$_2$Re[η^2-O=C(C$_6$H$_4$-*p*-CF$_3$)(C$_9$H$_7$O$_2$)] (5c). A CD_2Cl_2 solution of an equilibrium mixture of **2c**:**3c** was exposed to air and monitored by ^{1}H NMR spectroscopy. **3c** disappeared over several hours and **2c** disappeared more slowly over 112 h to give a 67% yield of **5c**. Preparative TLC (silica gel, 3:2 pentane/ether) gave **5c** ($R_f = 0.18$) as a yellow-brown solid. IR (THF): 2001 (C≡O), 1929 (C≡O) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.90 (br s, 2H), 7.65−7.58 (m, 4H), 7.52 (td, $J = 7.2, 1.2$ Hz, 1H), 7.45 (td, $J = 7.5, 1.5$ Hz, 1H), 5.19 (s, Cp), 2.65 (s, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 205.7 (ReCO), 201.4 (ReCO), 199.8 (C=O), 197.8 (C=O), 148.1, 139.9, 136.9, 132.3, 130.3, 128.6 (q, $J_{CF} = 33$ Hz), 127.8 (v br, 2C), 127.0, 125.2 (q, $J_{CF} = 3.6$ Hz, 2C), 125.0 (q, $J_{CF} = 272$ Hz), 93.1 (Cp), 76.2 (CORe), 27.7 (Me). HRMS (ESI): calcd for $C_{24}H_{16}F_3O_5{}^{185}$ReNa (M + Na$^+$) 649.0377, found 649.0366.

^{17}O-Labeled Cp(CO)$_2$Re[η^2-O=C(C$_6$H$_5$)(C$_9$H$_7$O$_2$)] (5a). Dioxygen that was 10% ^{17}O enriched was added

to a resealable NMR tube containing an equilibrium mixture of **2a**:**3a** in CD_2Cl_2. After 12 h, NMR spectroscopy showed that **2a** and **3a** had been consumed. Labeled **5a** was purified by preparative TLC and was shown to be pure by ^1H NMR spectroscopy. An ^{17}O NMR spectrum of labeled **5a** (~30 mM in CD_2Cl_2) was obtained by acquiring 1.8×10^5 scans with an acquisition time of 0.01 s and a repetition delay of 0 s. Varying the acquisition and delay times had little effect on the relative peak sizes. δ_O values are based on referencing to $CHDCl_2$ in the ^1H NMR spectrum and are reported relative to H_2O ($\delta_O = 0.0$ ppm). ^{17}O NMR (67.9 MHz, CD_2Cl_2): δ 564.6 (br s, 1.00 O, MeC═O), 510.4 (br s, 0.94 O, ArC═O).

^{17}O-Labeled Cp(CO)$_2$Re[η^2-O═C(C$_6$H$_4$CF$_3$)-(C$_9$H$_7$O$_2$)] (5c). Dioxygen that was 10% ^{17}O enriched was added to a resealable NMR tube containing an equilibrium mixture of **2c**:**3c** in toluene-d_8. After 36 h, labeled **5c** was purified by preparative TLC and was shown to be pure by ^1H NMR spectroscopy. An ^{17}O NMR spectrum of labeled **5c** was obtained by acquiring 8.3×10^5 scans with an acquisition time of 0.01 s and a repetition delay of 0 s. δ_O values are based on referencing to $CHDCl_2$ in the ^1H NMR spectrum and are reported relative to H_2O ($\delta_O = 0.0$ ppm). ^{17}O NMR (67.9 MHz, CD_2Cl_2): δ 564.6 (br s, 1.00 O, MeC═O), 509.1 (br s, 0.95 O, ArC═O).

^{17}O NMR Spectrum of 1,2-Diacetylbenzene. A natural abundance (0.037%) ^{17}O NMR spectrum of 1,2-diacetylbenzene (1.2 M in CD_2Cl_2) was obtained in 5.7×10^4 scans using an acquisition time of 0.003 s and a repetition delay of 0 s. The δ_O value is based on referencing to $CHDCl_2$ in the ^1H NMR spectrum and is reported relative to H_2O ($\delta_O = 0.0$ ppm). ^{17}O NMR (67.9 MHz, CD_2Cl_2): δ 563.5 (s).

Rhenium η^2-Benzil Complex Cp(CO)$_2$Re[η^2-O═C(C$_6$H$_5$)(C═O(C$_6$H$_5$))] (6). A solution of $CpRe(CO)_3$ (0.282 g, 0.841 mmol) in dry degassed THF (140 mL) was photolyzed with a Hanovia medium-pressure mercury lamp for 30 min at 0 °C with continuous N_2 purging. Benzil (C_6H_5(C═O)(C═O) C_6H_5) (1.77 g, 8.41 mmol) was added, and the solution was concentrated to 15 mL on a rotary evaporator. The brown solution was stirred under N_2 at 0 °C and was allowed to warm to room temperature and stirred for 22 h. Preparative TLC (silica gel, 2:1 pentane/ether) gave **6** (40.2 mg, 9.2%, $R_f = 0.32$) as an air-stable, yellow-orange powder. IR (THF): 2000 (s, C≡O), 1928 (s, C≡O), 1652 (m, C═O) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.95−7.89 (m, 4H), 7.45 (tt, $J = 7.2$, 1.2 Hz, 1H), 7.347 (t, $J = 8.1$ Hz, 2H), 7.344 (t, $J = 8.1$ Hz, 2H), 7.21 (tt, J 7.2, 1.2 Hz, 1H), 5.27 (s, 5H, Cp). ^{13}C {^1H} NMR (126 MHz, CD_2Cl_2): δ 204.3 (ReCO), 199.3 (ReCO), 198.5 (C═O), 142.4, 137.4, 132.3, 129.2 (2C), 128.4 (2C), 128.1 (2C), 127.5, 127.3 (2C), 92.7 (Cp), 78.1 (C(O)Re). A natural abundance (0.037%) ^{17}O NMR spectrum of benzil (0.2 M in CD_2Cl_2) was obtained in 1.5×10^7 scans using an acquisition time of 0.01 s and a repetition delay of 0 s. The δ_O value is based on referencing to $CHDCl_2$ in the ^1H NMR spectrum and is reported relative to H_2O ($\delta_O = 0.0$ ppm). ^{17}O NMR (67.9 MHz, CD_2Cl_2): δ 523.0 (br s, C═O), 379.8 (s, C≡O), 377.2 (s, C≡O), 144.3 (br s, C(O)Re). HRMS (ESI): calcd for $C_{21}H_{15}O_4{}^{187}ReNa$ ($M + Na^+$) 541.0426, found 541.0400.

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Supporting Information Available: X-ray crystallographic data for compounds **4c** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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