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First Direct Structural Comparison of Complexes of the Same Metal Fragment to Ketenes in Both C,C- and C,O-Bonding Modes

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Abstract: Using a series of Ir(I) and Rh(I) ketene complexes, conclusions about the structure and bonding of complexes of the fundamentally important ketene ligand class are reached. In a unique comparison of X-ray structures of the same metal fragment to ketenes in both the η^2-(C,C) and the η^2-(C,O) binding mode, the Ir−Cl bond distances in complexes of *trans*-Cl(Ir)[P(*i*-Pr)$_3$]$_2$ to phenylketene [**4**, η^2-(*C,C*)] and diphenylketene [**2a**, η^2-(*C,O*)] are 2.371(3) and 2.285(2) Å, respectively. This would be consistent with greater trans influence of a ketene ligand bound to a metal through its C=C bond than one connected by its C=O bond. Back-bonding of Ir(I) and Rh(I) to diphenylketene was assessed using *trans*-Cl(M)[P(*i*-Pr)$_3$]$_2$[η^2-(*C,O*)-diphenylketene] (**2a** and **2d**). Most bond lengths and angles are identical, but slightly greater back-bonding by Ir(I) is suggested by the somewhat greater deformation of the ketene C=C=O system [C−C−O angles are 136.6(4) and 138.9(4) in the Ir and Rh cases **2a** and **2d**, respectively]. Syntheses of new labeled ketenes Ph$_2$C=^{13}C=O and Ph$_2$C=C=^{18}O and their Ir(I) and Rh(I) complexes are reported, along with the generation of an Ir(I) complex of PhCH=^{13}C=O. The effects of isotopic substitution on infrared absorption data for ketene complexes are presented for the first time. Preliminary normal coordinate mode analysis allowed definitive assignment of absorptions ascribed to the C−O stretching frequencies of coordinated ketenes, which are near the absorptions for aromatic ring systems commonly found as substituents on ketenes. For free diphenylketene and four of its complexes and a phenylketene complex characterized by X-ray diffraction, the magnitude of the ^{13}C−^{13}C coupling between the two ketene carbons is correlated to carbon−carbon bond distance.

Introduction

Ketenes are versatile reaction partners in cycloadditions and nucleophilic addition reactions.[1−3] Coordination of a metal fragment to the ketene leads to an even wider range of possible structure and reactivity.[4] Ketene−metal complexes have been suggested as key intermediates in many of the applications of carbene−CO complexes to organic synthesis, including benzannulation reactions,[5] β-lactam or cyclobutanone formation,[6−8] and electrophilic substitution reactions.[9] However, in the reactions just cited, intermediate ketene complexes are inferred rather than observed directly. The lack of structural information makes it difficult or impossible to explain results such as changes in cyclization diastereoselectivity with changes in metal fragment.[7] The work reported here is part of our program to understand trends in structure, bonding,[10] and reactivity[11−14] of metal−ketene complexes.

In one class of ketene complexes involving a single metal, the metal imparts inertness to the ketene ligand.[15−17] A second class of ketene complexes are barely stable enough to be isolated, forming at temperatures of −20 to +50 °C mixtures of products that can be rationalized by cleavage of the ketene C=C bond.[18−21] Finally, a third kind of ketene complexes, too

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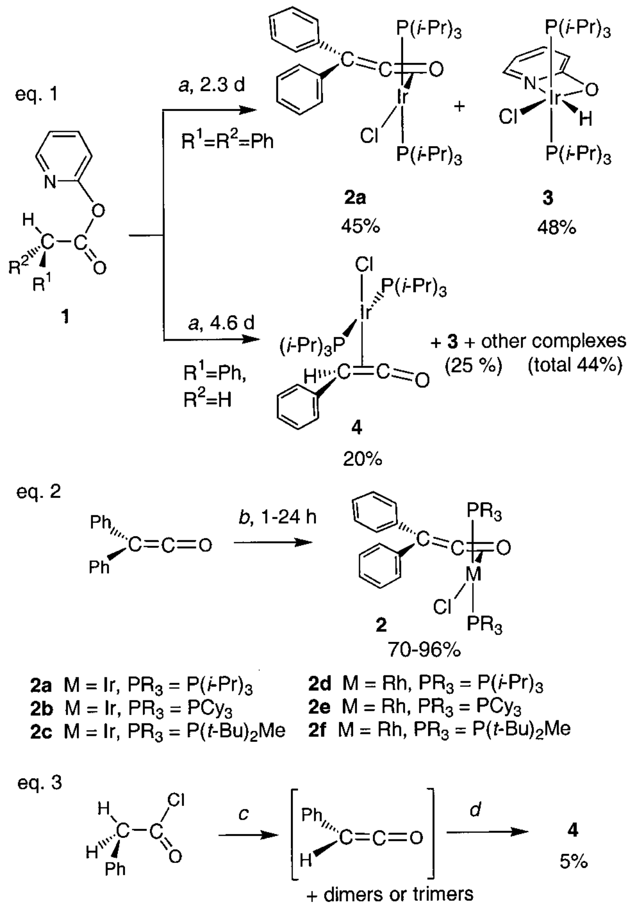
reactive to be isolated or even detected, have been proposed as reaction intermediates.[5,22−24] In contrast, Ir(I) and Rh(I) ketene complexes such as those reported here are unique in that they are stable enough to be isolated and characterized fully,[10] yet reactive.[11−14] In the work described here, we use the relative stability of a series of complexes to explore the structural and electronic effects of metal coordination at either the C,C or C,O bond. Relatively strong absorptions for ketenes and their complexes in infrared spectra make such data a useful tool in identifying the position of the metal on the ketene ligand.[4] These data have relevance not only to organometallic chemistry but also to surface science, where absorbed ketene has been identified using infrared spectroscopies.[25−27] As far as we are aware, the studies here include the first verification of assignments of C−O stretching frequencies, using isotopically labeled compounds.

Results and Discussion

Synthesis of Complexes. In 1995 we reported a preparation of the first Ir(I) ketene complexes, including **2a** and **4**, by metal-induced elimination reactions of 2-pyridyl esters **1** (Scheme 1).[10] This route is unique, because there are only two previous reports of ketene formation from transition metals and carboxylic acid derivatives (acid chlorides), and in these cases the reactions led to *free* ketenes,[28,29] a net result that one also can obtain in many cases by reaction of an acid chloride with a tertiary amine base.[2] In contrast, the chemistry portrayed in the upper part of Scheme 1 leads to ketene *complex* **2a** or **4**,[10] along with at least one other Ir-containing product, pyridinato complex **3**, the structure of which has been determined by X-ray crystallography.[30] The fragmentation of **1** gives access to a variety of iridium−ketene complexes, in which the ketene ligand has either two aryl groups, one aryl and one alkyl group, or, albeit in lower yields, only one aryl or alkyl group.[31] Subsequently it was found that a high yield of diphenylketene complex **2a** also could be obtained by a ligand substitution reaction (Scheme 1, eq 2) on $[(\mu\text{-Cl})Ir(cyclooctene)_2]_2$ using (per iridium) 2 mol of phosphine and 1 mol of diphenylketene[32] (which can be stored in the glovebox freezer for months without decomposition). This direct synthesis was used to make all six diphenylketene complexes (**2a**−**f**, eq 2 and Table 1) reported in this paper, along with several isotopomers, in yields of 70−96%. While this work was progress, a similar synthesis of Rh complex **2d** was reported.[33]

Scheme 1



[a] Conditions: $[Ir(\mu\text{-Cl})(cyclooctene)_2]_2$, 4 $P(i\text{-}Pr)_3$, C_6D_6, room temperature. [b] Conditions: 0.5 $[M(\mu\text{-Cl})(cyclooctene)_2]_2$, 2 $P(i\text{-}Pr)_3$, C_6H_6 or C_6D_6, room temperature. [c] Conditions: Et_3N, Et_2O, 0 °C, 8 h. [d] Conditions: 0.5 $[Ir(\mu\text{-Cl})(cyclooctene)_2]_2$, 2 $P(i\text{-}Pr)_3$, C_6H_6, room temperature, 10 min. To allow for consumption of phenylketene through oligomerization, 9−10 mol of $PhCH_2COCl$/mol of Ir was used.

Unfortunately, direct synthesis by ligand exchange works well only when stable ketenes and stable metal fragments or their precursors are used. Therefore, as far as we can tell, no one has used this route with monosubstituted ketenes.[31] As a demonstration of the difficulties encountered, phenylketene has only been characterized when made in inert matrixes at temperatures below 40 K,[34,35] as a transient solution species in flash photolysis reactions,[36,37] or when generated in the gas phase,[38,39] because of its facile oligomerization reactions.[40−42] When used preparatively, phenylketene is always generated in

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Table 1. Selected Spectroscopic Data for Complexes of Diphenylketene to Fragments *trans*-ClM(PR$_3$)$_2$ (δ in ppm, J in Hz)

	M	PR$_3$	^{31}P{^{1}H} (C$_6$D$_6$ solvent)	Ph$_2$C(2)=C(1)=O ^{13}C{^{1}H} (CDCl$_3$ or C$_6$D$_6$ solvent)^a		^{1}H of ortho protons of substituents (C$_6$D$_6$ solvent)		IR (cm^{-1})^d
				C(2)	C(1)	Ph syn to M (2 H)	Ph anti to M (2 H)	
2a	Ir	P(i-Pr)$_3$^{b,c}	20.90 (s)	74.75 (s)	143.78 (t, $J = 3.2$)	8.63 (d, $J = 7.2$)	7.63 (d, $J = 7.2$)	1636, 1589, 1493 (KBr)
2b	Ir	PCy$_3$	10.99 (s)	74.42 (s)	142.33 (t, $J = 3.7$)	8.66 (d, $J = 7.2$)	7.84 (d, $J = 7.2$)	1627, 1591, 1441 (C$_6$D$_6$)
2c	Ir	P(t-Bu)$_2$Me	17.85 (s)	76.01 (s)	138.18 (t, $J = 3.9$)	8.42 (d, $J = 8.0$)	7.64 (d, $J = 8.0$)	1624, 1591, 1471 (C$_6$D$_6$)
2d	Rh	P(i-Pr)$_3$	32.55 (d, $J = 112.0$)	77.06 (d, $J = 2.1$)	167.77 (dt, $J = 20.1, 5.6$)	8.76 (d, $J = 7.5$)	7.65 (d, $J = 7$)	1656, 1599, 1590, 1494, 1461, 1446 (KBr)
2e	Rh	PCy$_3$	22.57 (d, $J = 107.1$)	77.25 (d, $J = 3.0$)	167.58 (dt, $J = 20.2, 4.6$)	8.75 (d, $J = 7.6$)	7.87 (d, $J = 7.6$)	1645, 1589, 1444 (C$_6$D$_6$)
2f	Rh	P(t-Bu)$_2$Me	31.97 (d, $J = 109.1$)	79.17 (d, $J = 2.3$)	165.13 (dt, $J = 20.7, 5.8$)	8.57 (d, $J = 8.4$)	7.64 (d, $J = 8.2$)	1650, 1594, 1475 (C$_6$D$_6$)

[a] **2b** and **2c** in CDCl$_3$, **2a**, **2d**−**2f** in C$_6$D$_6$. [b] Reference 10. [c] Reference 11. [d] See also Table 6.

the presence of the desired reactant.[43,44] In this study, because acid chlorides oxidatively add to Ir(I)−phosphine complexes,[45,46] direct synthesis of phenylketene complex **4** required generation of phenylketene in solution by allowing phenylacetyl chloride to react with triethylamine at 0 °C for 4 h, followed by filtration of the resulting mixture into a solution of the metal fragment. While less efficient than the fragmentation of pyridyl ester **1** (R^1 = Ph, R^2 = H) route in terms of yield, this protocol was significantly faster, allowing synthesis of phenylketene complex **4** within 1 day in 5% yield. After completion of this part of our study, Tidwell and co-workers reported a promising alternative method of making dilute solutions of phenylketene in hydrocarbon solvent,[47] which may be useful in improving the yield of **4** and related species.

The identification of the ketene complexes was eventually confirmed by X-ray diffraction (vide infra) but was suggested by a combination of NMR and IR spectral data (Table 1). For the diphenylketene complexes **2a**−**f**, the ^{31}P{^{1}H} NMR spectra show a single resonance, a singlet in the case of the Ir species and a doublet ($^1J_{\mathrm{PRh}}$ = 107.1−112.0 Hz) in the Rh cases. The magnitude of the Rh−P coupling constant is consistent with a Rh(I) species with mutually trans phosphines sharing the same metal orbital. Two linkage isomers of these complexes are possible,[33] the η^2-(C,O) complexes shown or alternative η^2-(C,C) isomers. Particularly diagnostic is the fact that the ^{1}H and ^{13}C NMR spectra of **2a**−**f** show two inequivalent phenyl rings, consistent with metal coordination to one side of the C,O bond. Alternative η^2-(C,C) isomers would feature equivalent phenyl rings. The nuclei of the phenyl rings experience different shielding: the ortho protons of the phenyl ring syn to the metal resonate in the range δ 8.42−8.76 ppm whereas those anti resonate upfield, between δ 7.63 and 7.87 ppm.[48]

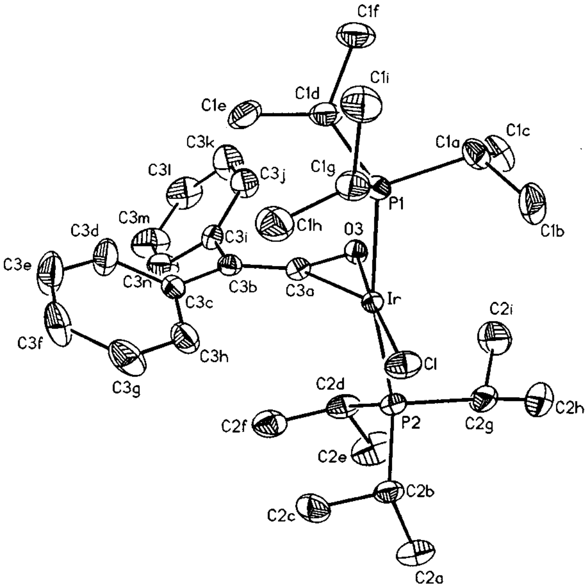

Figure 1. Molecular structure of **2a**. See Table 2 for key bond lengths and angles.

In contrast, **4** was formulated as the η^2-(C,C) isomer shown. The ^{31}P{^{1}H) NMR spectrum of the complex showed two doublets at δ 25.43 and 23.30 ppm, each with a large coupling constant $^2J_{\mathrm{PP}}$ = 323.5 Hz, consistent with the presence of mutually trans phosphines. Only the η^2-(C,C) isomer, which features planar chirality, would have two inequivalent trans phosphines; the two alternative η^2-(C,O) isomers, one with the phenyl group syn, the other anti to the metal fragment, would be achiral and would contain equivalent phosphines.

The ^{13}C NMR and IR spectral data for these species will be discussed in detail below.

X-ray Crystallography. X-ray diffraction studies verified the assignments just described, but more significantly, gave insight into metal−ketene bonding. The molecular structures of **2a** (Figure 1) and **2d** have been communicated by us[10] and by Werner's group,[33] respectively. Because **2a** and **2d** feature the same ligand set, most of this paragraph will compare these two species. The structure of **2c** is new (Figure 2). For all three structures, selected bond lengths and angles are shown in Table 2. In each case, the complexes show essentially square planar geometry. The square plane can be roughly defined by the metal and the ligating atoms Cl, P, and P, with the O atom of the ketene closest to that plane. In **2a** and **2d** the P−Ir−P angles are 168.0(1) and 168.41(4)°, respectively, and a plane defined

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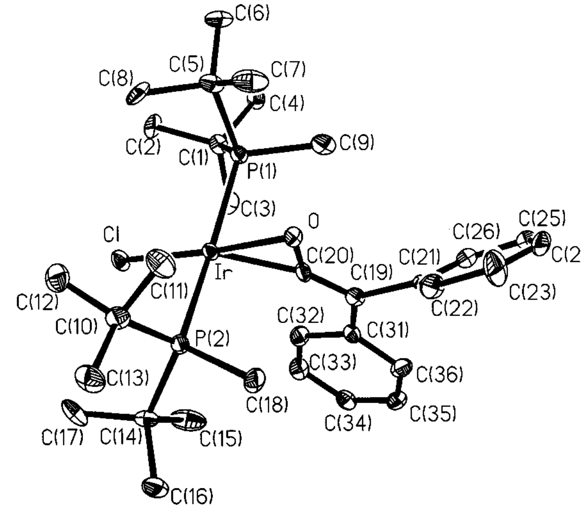

Figure 2. Molecular structure of **2c**. See Table 2 for key bond lengths and angles.

Table 2. Comparison of the Geometries of **2a**, **2d**, **2c**, and $Ph_2C{=}C{=}O$ (bond distances in Å, Angles in deg)

parameter[a]	**2a**[b]	**2d**[c]	$Ph_2C{=}C{=}O$[d]	**2c**[e]
C(1)−C(2)	1.348(6)	1.349(6)	1.333	1.356(16)
C(1)−O	1.286(6)	1.264(5)	1.188	1.295(12)
C(1)−M	1.972(5)	1.971(4)		1.982(12)
O−M	2.092(4)	2.090(3)		2.099(8)
M−Cl	2.285(2)	2.298(1)		2.300(6)
M−P	2.366(2), 2.381(2)	2.369(1), 2.382(1)		2.362(3), 2.283(3)
C(2)−C(1)−O	136.6(6)	138.9(4)		134.3(10)
C(2)−C(1)−M	146.7(5)	144.0(3)		148.9(8)

[a] Numbering of ketene atoms in parameter column same for all structures [$Ph_2C(2){=}C(1){=}O$]. [b] Reference 10. [c] Reference 33. [d] From semiempirical AM1 calculations.[38] [e] This work.

by the metal atom and the two phosphines passes through the phenyl ring syn to the bulky metal fragment, consistent with repulsive steric interactions between metal fragment and the nearest ketene phenyl substituent. Key bond distances and angles in these complexes are virtually identical (Table 2), showing strong distortion from calculated values for the free ligand diphenylketene.[38] The slight differences between complexes of the two metals would be consistent with mildly greater back-bonding in the Ir complex than in the Rh analogue. The C−C−O angle in the Ir(I) species is 136.6(4)°, whereas in the Rh analogue, the deformation from linear geometry is less [138.9(4)°]. Moreover, the M−C−C angle in the Ir complex is 2.7° greater than in the Rh analogue. The data are all within the ranges shown by other metal complexes featuring diphenylketene bound in an η^2-(C,O) fashion.[4,49−52] Finally, we observe that the structure of **2c** is similar to that of **2a**, with the notable difference that the phosphine ligands are oriented to place the sterically unassuming methyl groups closer to the ketene ligand.

Because there is no example of crystal structures of the same metal fragment to ketenes in different binding modes, it was of great interest to obtain a structure for **4**. A crystal of complex **4** suitable for X-ray diffraction studies was analyzed at −100 °C. The molecular structure of the compound is shown in Figure 3, and selected bond distances and angles are given in Table 3. As far as we are aware, this is the first crystal structure of a η^2-(*C,C*)-monosubsituted ketene complex. The complex exhibits slightly distorted square planar geometry about the Ir atom, as revealed by a 359.6° sum of four angles between Cl, P(1), P(2), and C(27) and the central Ir atom. Atoms P(1), P(2), Cl, and C(27) lie in a plane with an average deviation on 0.070 Å. Inclusion of the central Ir atom in this calculation gives almost the same result, a deviation of 0.075 Å. Thus, in **4**, the ketene carbon atom C(27) is closest to the square plane, whereas in **2a**, **2c**, and **2d**, it is the ketene oxygen that is closer. In **4**, the plane containing the C═C═O atoms is nearly perfectly perpendicular (92.3°) to the square plane defined above. The P−Ir−P angle of 166.6(1)° and the direction of distortion from the ideal 180° value suggest that the phosphines are oriented to minimize steric interactions with the phenylketene ligand. This impression is reinforced by the fact that the phosphine syn to the phenyl ring [P(2)−Ir−C(27) angle, 99.8(3)°] appears to be displaced more than the phosphine anti to the phenyl group [P(1)−Ir−C(27) angle, 89.7(3)°]. The displacement of the phosphine syn to the phenyl ring is also shown by the fact that the distance between C(27) and P(2) is 3.476 Å, 0.265 Å greater than the distance between C(27) and P(1), and the distance between C(28) and P(2) (3.336 Å) is 0.211 Å greater than that between C(28) and P(1). Finally, we note that in both **4** and **2a**/**2c**/**2d** the metal−phosphorus bond lengths are similar, whereas the metal−chlorine bond length in **4** is significantly longer (2.371 vs 2.285−2.300 Å). This difference may be attributed to a greater trans influence of the ketene when bound at the C,C bond, assuming that the electronic perturbation of one phenyl substituent is insignificant.

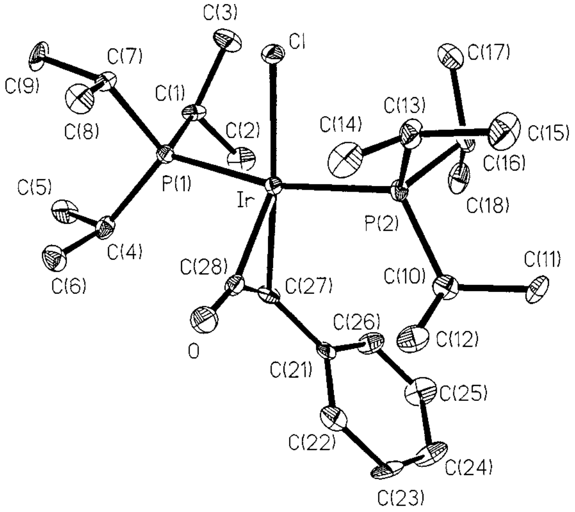

Figure 3. Molecular structure of **4**. See Table 3 for key bond lengths and angles.

Only theoretically calculated geometries are available for the free phenylketene ligand,[38,53] but it is clear that, in complex **4**, the C(27)−C(28) bond is elongated [1.468(17) Å in **4** vs 1.311[38] or 1.319[53] Å in phenylketene] and the C═C═O unit is bent due to back-bonding (see below). The C−O bond distance is not much different [1.165(13) vs 1.145[38] or 1.190[53] Å].

There are five other crystal structures of ketene complexes featuring η^2-(C,C) coordination, and these all involve di-

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4

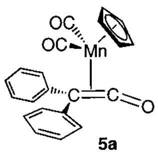
Ir−Cl	2.371(3)	C(28)−O	1.165(13)	P(2)−Ir−C(27)	99.8(3)
Ir−P(1)	2.378(3)	P(1)−Ir−P(2)	166.6(1)	Cl−Ir−C(27)	174.9(3)
Ir−P(2)	2.370(3)	Cl−Ir−P(1)	85.6(1)	Cl−Ir−C(28)	140.9(4)
Ir−C(27)	2.171(11)	Cl−Ir−P(2)	84.5(1)	Ir−C(28)−O	139.1(10)
Ir−C(28)	1.935(11)	Cl−Ir−C(27)	174.9(3)	C(27)−C(28)−O	142.6(12)
C(27)−C(28)	1.468(17)	P(1)−Ir−C(27)	89.7(3)		

Table 4. Structural Data for Known η^2-(*C*,*C*)-Bound Ketene Complexes [Bond Distances (Å) and Angles (deg), Ketene Numbering $R_2C(2){=}C(1){=}O$]

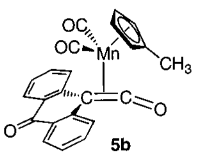
complex	C(1)−C(2)	C(1)−O	C(2)−C(1)−O	M−C(1)	M−C(2)	ref
5a	1.35(2)	1.21(2)	145	1.96(2)	2.17(2)	15
5b	1.448(8)	1.194(8)	139.8(6)	1.976(6)	2.242(6)	54
5c	1.401(9)	1.224(8)	142.5(7)	1.940(7)	2.212(6)	55
6	1.467(5)	1.208(4)	142.0(5)	1.936(5)	2.180(5)	33
4	1.468(17)	1.165(13)	142.6(12)	1.935(11)	2.171(11)	*a*
7	1.488(7)	1.222(6)	141.3(5)	1.986(5)	2.245(4)	14

[a] This work.

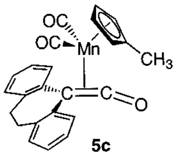
arylketenes (Table 4). From 1976 to 1984, three structures of diarylketene complexes (**5a**−**c**) with metal fragments of the type η^5-$(C_5H_4R)Mn(CO)_2$ were reported by Herrmann and coworkers,[15,54,55] and in 1999 a structure of η^5-(indenyl)Rh[P(*i*-Pr)$_3$] coordinated to the C,C bond of diphenylketene (**6**) was published by Werner and co-workers.[33] (Although the C,O-bound linkage isomer of **6** was prepared,[33] its crystal structure is unfortunately not available for comparison.) Finally, we recently described the structure of complex **7**.[14] The reported structures resemble that of **4** in that the C═C bond of the coordinated diarylketenes are elongated and the C═C═O unit is bent. The Rh(I) and Ir(I) examples exhibit the greatest degree of deformation.



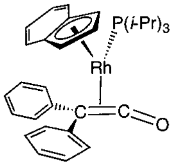
5a



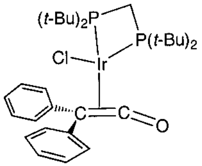
5b



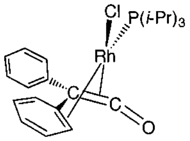
5c



6



7



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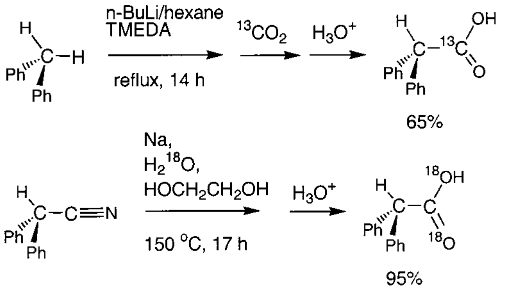
In summary, comparing the X-ray structure of complex η^2-(*C*,*O*)-phenylketene complex **4** with those of η^2-(*C*,*O*)-diphenylketene complexes **2a**, **2c**, and **2d** reveals the following similarities: (a) there is significant back-bonding from the metal to the ketene π-system, with concomitant elongation of the coordinated π-bond and bending of the ketene ligand away from the metal; (b) distortions consistent with steric interactions between ketene and phosphine substituents are seen. Differences between the two types of complexes include (a) a longer metal−chlorine bond when then ketene trans to Cl is bound at the C,C bond and (b) a greater elongation of the attached multiple bond in the case of the C,C bond than the C,O bond. These observations do nothing to contradict our earlier conclusion[10] that there is an electronic preference for binding of the ketene to the C,C bond, which may be overridden by steric factors and lead to C,O-binding. Most significant, however, is the observation of the longer Ir−Cl bond in **4** compared to that in **2a**. Although the origins of the trans influence are a subject of continuing debate,[56] if one assumes that phenyl and diphenylketene are electronically similar, *our structures suggest that a ketene is a better π-acid when bound through the C,C bond.*

Scheme 2



To investigate bonding in the complexes more fully, a series of ^{13}C NMR and IR spectroscopic investigations was performed. For this work, new isotopically labeled ketenes and their precursors were required, as described in the next section.

Syntheses of Isotopically Labeled Ketenes and Their Complexes. Both ^{13}C- and ^{18}O-labeled ketenes were needed for the IR and NMR studies conducted. The diphenylketene isotopomer $Ph_2C{=}^{13}C{=}O$ was unknown. $Ph_2C{=}C{=}^{18}O$ has been reported once,[57] but as a product of a rather indirect synthesis and without spectroscopic data. Furthermore, the sample produced had only 4% isotopic enrichment. However, for our purposes we sought to prepare diphenylketene with a high degree of isotopic enrichment. This in turn required highly enriched samples of diphenylacetic acid as a precursor. The acid $Ph_2CH^{13}CO_2H$ has been mentioned in the literature,[58] but without details of its preparation. In the present work (Scheme 2), diphenylmethane was deprotonated using BuLi−TMEDA and the resulting mixture added to a flask containing $^{13}CO_2$ at 1 atm pressure. Acid workup afforded $Ph_2CH^{13}CO_2H$ in 65% yield. Similarly, monophenyl precursor $PhCH_2{}^{13}CO_2H$ was obtained in 67% yield or purchased. The sample of $^{13}CO_2$ used to make the two acids was 99% enriched in ^{13}C but also contained a few percent ^{18}O, so in some NMR and IR spectra of the products and subsequent intermediates, additional satellites for the $^{13}C^{18}O$ isotopomer could be seen. Finally, isotopomer $Ph_2CHC(^{18}O)_2H$ was produced by base-catalyzed hydration of the nitrile Ph_2CHCN in $H_2{}^{18}O$. This and all other isotopically labeled acids were converted to the ketenes using $SOCl_2$, followed by Et_3N.[59] Complexation proceeded as for the unlabeled ketenes.

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Table 5. Comparison of Carbon−Carbon Coupling Constants and Bond Distances

species	$^1J_{CC}$ (Hz)	C−C bond distance (Å)[a]	ref for C−C distance
$Ph_2C{=}C{=}O$	107[b]	1.333	38
2a	92.5[b]	1.348(6)	10
2d	93.0[c]	1.349(6)	33
8	54.4[d]	1.442(6)	13
4	45.7[c]	1.468(17)	*e*
7	44.3[d]	1.488(7)	14

[a] Values from X-ray diffraction, except for $Ph_2C{=}C{=}O$, which comes from semiempirical AM1 calculations. [b] $CDCl_3$, 30 °C. [c] C_6D_6, 30 °C. [d] CD_2Cl_2, −50 °C. [e] This work.

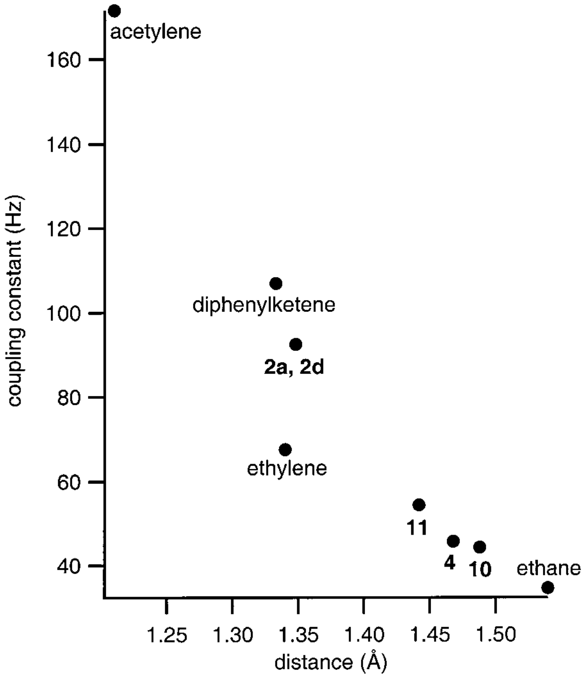

Figure 4. Plot of $^1J_{CC}$ and C−C bond distance. All values are experimentally determined, except for the calculated bond distance for $Ph_2C{=}C{=}O$. See Table 5 for data on ketene derivatives.

NMR Spectroscopy. The proton NMR shifts for related Ir and Rh complexes are virtually identical, but significant differences in ^{13}C NMR chemical shifts of the ketene C(1) carbon are seen (Table 1). The ^{13}C NMR chemical shifts for the C(1) carbon in the Rh complexes (δ 165.13−167.77 ppm) are closer to that in the free ligand (δ 201.2 ppm)[2,60,61] than those of the Ir analogues (δ 138.18−143.39 ppm). As analyzed above, the X-ray structures of Ir and Rh complexes **2a** and **2d** suggested slightly greater back-bonding in the Ir congener. However, examination of the literature suggests that differences in ^{13}C NMR data are due to some effect other than back-bonding.[62] Recent work on the effects of heavy atoms on NMR chemical shifts suggests that the greater spin−orbit coupling in the third-row metal may be responsible for the shielding effect.[63]

To characterize the degree of back-bonding further, the magnitude of $^1J_{C(1)-C(2)}$ between the two ketene carbons was determined. Although in principle natural abundance materials could be analyzed in this way using the INADEQUATE pulse sequence, the relatively low sensitivity obtainable has led in other studies to the use of as much as 2 g of metal complex.[64] In our work, the expense of Ir and Rh and the difficulty in obtaining more than 100 mg of **4** for study prompted synthesis of ketene complexes enriched with ^{13}C (vide supra); moreover, isotopically labeled materials were needed for IR spectroscopy (vide infra). Table 5 compares $^1J_{CC}$ values (all new data) and C−C bond distances for $Ph_2C{=}C{=}O$, for four of its complexes, and for $PhCH{=}C{=}O$ complex **4**. Inspection of the data shows that $^1J_{CC}$ decreases as the C−C bond distance increases, results shown in Figure 4 along with literature data for ethane, ethene, and ethyne.[65] Among ethene and ethyne complexes, some correlation between C−C bond distance and $^1J_{CC}$ has been seen,[64,66] but the data here are the first reported for ketene complexes. For organic molecules, it is agreed that the magnitude of $^1J_{CC}$ is dominated by the Fermi contact interaction, which in turn depends on the electron densities at the two carbons.[66] Thus, as originally formulated by Frei and Bernstein,[67] $^1J_{CC} = a(s_{C1} \times s_{C2}) + b$, where s_{C1} and s_{C2} refer to the amount of *s* character of the carbon atoms of the ketene ligand. Our data would allow only for calculation of the product $s_{C1} \times s_{C2}$.

To further probe how metal coordination to the ketene π-system may change the hybridization of the carbons, the spin−spin coupling between the terminal ketene carbon C(2) and attached proton was considered. In other π-systems, the effect of metal coordination on $^1J_{CH}$ values varies. In arene and cyclopentadienyl compounds, $^1J_{CH}$ increases on metal coordination, whereas in η^2-(*C,C*)-alkene complexes, it decreases. The causes of the former change are unclear, but for the latter, a reduction in carbon s-character through metal−ligand back-bonding has been offered as explanation.[65] Therefore, because complex **4** featured a hydrogen on the ketene π-system, a gated decoupling ^{13}C NMR experiment was performed, allowing observation of $^1J_{CH} = 158$ Hz. Similar data on the free phenylketene ligand are unavailable because of the cumulene's instability. As far as we are aware, the only data for ketenes in the literature are $^1J_{CH} = 171.5$ and 184.4 for $H_2C{=}C{=}O$[60,61] and $H(Cl)C{=}C{=}O$,[68,69] respectively. In comparison, we note that, for η^2-(*C,C*)-$(H_2C{=}C{=}O)Pt(PPh_3)_2$, $^1J_{CH} = 159$ Hz.[19] These values compare with 156.4 Hz in ethylene, 154.5 Hz for the α C−H bond in styrene, and 167.8 Hz in allene.[65] If the

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(60) Firl, J.; Runge, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 668−669.

(61) Firl, J.; Runge, W. *Z. Naturforsch., B* **1974**, *29B*, 393−398.

(62) For example, in alkyl complexes there is no back-bonding from the metal to the alkyl ligand, yet in $Cp^*M(R)(H)(PMe_3)$, where R = cyclopentyl, the cyclopentyl carbon directly attached to the metal was shifted upfield in the Ir case (δ 0.22 ppm)[62a] compared to the Rh case (7.21 ppm).[62b] Similar effects were seen for the Cp* carbons attached to the metal (Ir, 92.37; Rh, 97.31 ppm) and for the phosphorus nuclei as well (Ir case, −44.83 ppm; Rh case, 9.5 ppm).[62a,62b] Furthermore, in hydride complexes (H)-$(Cl)_2M[P(i\text{-}Pr)_3]_2$, the hydride proton is more shielded in the Ir complex than in the Rh analogue (Ir−H, δ −48.83 ppm;[62c] Rh−H, δ −31.2 ppm[62d]). Similar trends have been noted (without comment) for metal carbonyls.[62e] Thus, the effect appears general and applies to ligands of many types. (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332−7346. (c) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407. (d) Harlow, R. L.; Thorn, D. L.; Baker, R. T.; Jones, N. L. *Inorg. Chem.* **1992**, *31*, 993−997. (e) Parish, R. V. *NMR, NQR, EPR, and Mössbauer Spectroscopy in Inorganic Chemistry*; Ellis Horwood: New York, 1990; p 72.

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(69) Lindner, E.; Steinwand, M.; Hoehne, S. *Chem. Ber.* **1982**, *115*, 2181−2191.

Table 6. IR Data for Isotopomers of Ir and Rh Ketene Complexes

species	conditions	$^{12}C{=}^{16}O$	$^{13}C{=}^{16}O$	$^{12}C{=}^{18}O$
$Ph_2C{=}C{=}O$	hexanes, NaCl cell, RT	2102 (s), 1599 (m), 1495(m), 1458 (s)	2046 (s), 1600 (m), 1494 (m)	2075 (s), 1599 (m), 1495 (m)
2a	CH_2Cl_2, −52 °C	1632 (s), 1589 (s), 1494 (m), 1464 (m)	1610 (m), 1581 (s), 1567 (s), 1494 (m), 1463 (m)	1626 (s), 1588 (s), 1493 (m), 1463 (m)
2a	KBr, RT	1636 (s), 1589 (s), 1493 (m), 1460 (m), 1445 (m)	1610 (m), 1582 (s), 1568 (s), 1494 (m), 1461 (m), 1443 (m)	1631 (s), 1590 (s), 1494 (m), 1461 (m)
2d	KBr, RT	1656 (s), 1599 (s), 1590 (s), 1494 (m), 1461 (m), 1446 (m)	1619 (s), 1590 (s), 1491 (m), 1463 (m)	nd[a]
	C_6D_6, NaCl cell, RT	1651 (s), 1591 (s), 1494 (s), 1468 (s), 1447 (s)	1617 (s), 1587 (s), 1491 (m), 1452 (s)	nd
4	CH_2Cl_2, −52 °C	1752 (s), 1708 (m), 1597 (m), 1489 (m), 1465 (m)	1719 (s), 1710 (s), 1678 (s), 1597 (s), 1490 (m), 1462 (m)	nd
8	C_6D_6, NaCl cell, RT	1801 (s), 1620 (s), 1455 (s)	1755 (s), 1737 (m), 1597 (w), 1476 (m), 1446 (m)	nd
7	CH_2Cl_2, NaCl cell, RT	1728 (s), 1591 (m), 1483 (s)	1693 (s), 1595 (w), 1491 (s), 1473 (m)	nd

[a] nd, not determined.

phenyl substituent on ketene has a similarly negligible effect as it does on ethylene, we would anticipate the coupling constant for phenylketene to be ~171.5 Hz, whereas in the complexed ligand it is 158 Hz. If the equation $^1J_{CH} = 570(s) - 18.4$ is used,[65] then in free and complexed phenylketene the s-character of C(2) would be 0.332 and 0.309, respectively. However, because of uncertainty regarding the theoretical meaning of changes in $^1J_{CH}$, the use of this equation for anything other than hydrocarbons has been questioned.[70]

The clearest conclusions from our work are that a good correlation between $^1J_{C(1)-C(2)}$ and the C(1)−C(2) bond distance can be established and that the chemical shifts of C(1) in ^{13}C NMR spectra of Rh and Ir complexes are upfield in the Ir series, probably because of relativistic effects.

Infrared Spectroscopy. IR data for Rh− and Ir−ketene complexes (Table 6) show the strong perturbation of the ketene ligand by the metal regardless of the position of binding. Whereas the C−O stretching frequency of coordinated ketenes shown in Table 6 is in the range 1600−1800 cm^{-1}, the corresponding absorption for the free ketenes appears near 2100 cm^{-1},[2] as assigned using ^{13}C- and ^2H-labeled ketene itself.[71−75]

However, IR data of the Rh− and Ir−ketene complexes show a significant difference: the absorption assigned to the C−O stretching appears in the range 1624−1636 (Ir) and 1645−1650 cm^{-1} (Rh). Although this band has been assigned routinely to the C−O stretch in a variety of diphenyl- and (phenyl)(alkyl)-ketene complexes in which a metal is coordinated to the C,O bond, the wide variance in the value for this stretching frequency (from a low of 1548 cm^{-1} to a high of 1632 cm^{-1})[18,49−52,76,77] and the overlap with absorptions of the aryl ring near 1580 cm^{-1} [78] prompted us to perform the first study of isotopically labeled ketene complexes.

In the spectra of **2a**, the intense band at 1632 cm^{-1} shifts to 1610 cm^{-1} upon ^{13}C substitution using $Ph_2C{=}^{13}C{=}O$; this peak is assigned to the diphenylketene C−O stretching mode. In the rhodium analogue, **2d**, the C−O stretching mode is attributed to the band at 1656 cm^{-1}, which shifts down in energy (1617 cm^{-1}) upon ^{13}C substitution.[79] When phenylketene is bound via the C═C bond, as in **2**, ν(CO) is found at 1752 cm^{-1} and decreases 33 cm^{-1} upon ^{13}C substitution using $PhCH{=}^{13}C{=}O$. Finally, substitution of the ketene oxygen with ^{18}O in **2a** also leads to lowering of the band by 6 cm^{-1} to 1626 cm^{-1}, which at first glance seemed a very modest shift. However, in η^2-(*C*,*O*)-acetone complexes, ^{18}O substitution lowers the C−O stretching frequency only from 1330 to 1312 cm^{-1} [80] or from 1230 to 1220 cm^{-1}.[81]

To better understand the proposed assignments for the ketene complexes, initial[82] normal coordinate analyses[83] of the vibrational modes of the metal−diphenylketene fragments were undertaken. Using calculated bond lengths and angles for diphenylketene and treating each phenyl ring as a point mass, the reported isotopic shifts of ν(CO) of free diphenylketene[2] can be fit very well to an approximate force field using the Wilson F and G matrix method.[84] To reproduce the selected vibrational frequency for Ph_2CCO, $Ph_2C^{13}CO$, $Ph_2CC^{18}O$, and $Ph_2{}^{13}CC^{18}O$, only two primary force constants are required (Table 7) suggesting kinematic coupling via the shared carbon atom but not necessarily electronic coupling of the C−C and C−O stretching modes. Upon binding diphenylketene to iridium via the C═O bond, the energy of the carbon−oxygen stretching mode decreases dramatically. In our model studies (Table 7) of the [M(η^2-Ph_2CCO)] (M = Ir, Rh) fragments and isoto-

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(79) In all of the complexes, there are also strong absorptions in the vicinity of 1590 cm^{-1}. The difficulty of using IR spectroscopy to assign metal position on highly substituted ketenes is shown by the recent assignment of the absorption of **2d** at 1590 cm^{-1} to the C−O stretching mode.[33] We have contacted Professor Werner, who agrees with our revised assignment.

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(81) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298−2308.

(82) For complex **2d**, the limited vibrational data preclude the possibility of a complete analysis of the vibrational modes. The reported force constants reflect a self-consistent analysis, but a number of force fields are possible. Refer to the Experimental Section for further details.

(83) Experimental data were fit using a nonlinear least-squares fitting program (Program QCMPO12, Quantum Chemistry Program Exchange; Indiana University, Bloomington, IN) that varied the primary force constants identified in the *F* matrix of the generalized valence force field (GVFF).

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Table 7. Experimentally Observed and Calculated Vibrational Frequencies and Calculated Force Constants

compd		vibrational frequencies (cm^{-1})				force constants[a] (mdyn/Å)			% symmetry coordinate in ν(CO)
		CCO	$C^{13}CO$	$CC^{18}O$	$C^{13}C^{18}O$	f_{CO}	f_{CC}	$f_{CC/CO}$	
Ph_2CCO	$\nu(CO)_{expt}$	2102	2046	2075	2019				
	$\nu(CO)_{calc}$	2102	2045	2076	2019	13.9	7.8	0.0	70 CO, 30 CC
2a	$\nu(CO)_{expt}$	1632	1610	1626					
	$\nu(CO)_{calc}$	1645	1600	1626		9.4	6.7	1.3	60 CO, 40 CC
2d	$\nu(CO)_{expt}$	1656	1617						
	$\nu(CO)_{calc}$	1655	1614			8.8	7.1	1.1	61 CO, 39 CC
7	$\nu(CO)_{expt}$	1728	1694						
	$\nu(CO)_{calc}$	1732	1692			11.7	4.2	0.7	97 CO, 2 CC
4	$\nu(CO)_{expt}$	1752	1719						
	$\nu(CO)_{calc}$	1760	1715			11.4	4.8	0.75	83 CO, 15 CC

[a] For each calculated set of force constants the M−L bond force constant was held to 1.5 mdyn/Å. Refer to Experimental Section for details.

pomers, the C−O and C−C stretching force constants decrease, while the C−C/C−O interaction force constant in each model is *increased* as a result of coordination to the metal. A positive interaction force constant indicates that as the C═O bond is lengthened, the strength of the C═C bond increases and, correspondingly, when the C═C bond is lengthened the C═O bond strength increases. As shown by the potential energy distributions of the carbon−oxygen stretching mode in the free and η^2-(C,O)-bound ketenes, the coupling of the C−C and C−O symmetry coordinates increases in the metal-bound diphenylketene fragment. When the C═C bond is coordinated to the metal center, as in **4** and **7**, the electronic coupling of the C═C and C═O symmetry coordinates decreases and the vibrational modes become more pure. As would be predicted by a simple harmonic oscillator approximation, the C═O bond stretching force constant increases in these complexes and the C═C bond stretching force constant decreases.

Conclusions

The first crystal structure of a monosubstituted ketene in η^2-(C,C) binding mode is presented in phenylketene complex **4**. Significantly, by comparing its crystal structure with that of η^2-(C,O)-diphenylketene complex **2a**, a longer Ir−Cl bond in **4** is taken as evidence that a η^2-(C,C)-bound ketene has a higher trans influence than a η^2-(C,O)-bound ketene. Five complexes of diphenylketene-1-^{13}C and one of phenylketene-1-^{13}C were made in order to analyze their IR and ^{13}C NMR spectra. From the structural and ^{13}C NMR data, a correlation between increased ketene C−C bond distance and decreased one-bond coupling constant can be made. Moreover, for the first time, IR data for coordinated ketenes were definitively assigned and normal coordinate mode analysis was used to assess the mixing of vibrational modes. These results should be useful in future studies of ketenes both in organometallic chemistry and in surface science, with impact on fields such as organic synthesis and catalysis.

Experimental Section

General Information. Reactions were performed in resealable NMR tubes (J. Young or Wilmad Glass) under dry nitrogen, using a combination of Schlenk line and glovebox techniques. C_6D_6 was distilled from $LiAlH_4$. Radial chromatography was carried out with a Harrison Research Chromatotron under a N_2 atmosphere; silica gel (SiO_2) and deoxygenated solvents were used. $^{13}CO_2$ was obtained from Cambridge Isotope Laboratories and contained 99% ^{13}C but, according to the manufacturer, also contained 5−7% ^{18}O.

Unless otherwise specified, ^{1}H, ^{13}C, and ^{31}P data were measured at 30 °C on a 200-MHz (50.3 MHz for ^{13}C and 80 MHz for ^{31}P) or nominal 500-MHz (499.9 MHz for ^{1}H, 125.7 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to residual solvent resonances (^{1}H NMR: δ 7.15 for C_6HD_5 and δ 7.27 for $CHCl_3$. ^{13}C NMR: δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$), where ^{1}H NMR chemical shifts are followed (in parentheses) by multiplicity, coupling constants J in hertz, and integration. For complex coupling patterns (e.g., dt, $J = 3.2$, 7.6 Hz, 1 H), multiplicities and coupling constants are listed in the same order, e.g., the doublet (d) is characterized by the smaller coupling, and the triplet (t) by the larger coupling. The abbreviations br and sl br designate broad and slightly broad signals, respectively. $^{31}P\{^1H\}$ NMR chemical shifts are referenced to external 85% H_3PO_4 (aq). ^{1}H and ^{13}C chemical shifts for **2a** and **4** are slightly different from those reported earlier[10] because of different reference values used in this work.

IR spectra at ambient temperatures were obtained on a Perkin-Elmer-1600 FTIR spectrometer. Samples were examined in C_6D_6 solutions in NaCl cells or in KBr pellets. Low-temperature spectra were acquired on a Mattson Research Series FTIR equipped with an external reflectance cell with a temperature sensor in the cell and a circulating cooling bath to cool the cell. Samples were injected as solutions ∼5 mM in complex in dry CH_2Cl_2. Elemental analyses were performed at NuMega Resonance Labs (San Diego, CA). High-resolution mass spectra were observed at the UC Riverside Mass Spectrometry Facility.

Representative Procedure for Preparation of *trans*-Cl(PR$_3$)$_2$(η^2-Ph$_2$C═C═O)M (M = Rh, Ir) (2a−f). *trans*-Chlorobis(tricyclohexylphosphine)(η^2-*C,O*-diphenylketene)rhodium (2e). A J. Young NMR tube was charged with [(μ-Cl)Rh(cyclooctene)$_2$]$_2$ (71.3 mg, 0.099 mmol) in a glovebox, and C_6D_6 (∼1.0 mL) was added to give a suspension. To this was added Ph$_2$C═C═O (49.0 mg, 0.252 mmol) via syringe. P(Cy)$_3$ (112.6 mg, 0.402 mmol) was then added. Upon the addition of P(Cy)$_3$, a clear red solution formed. The tube was sealed and shaken to mix the contents well before removal from a glovebox, and the tube was kept at room temperature, protected from light. The reaction was followed by ^{1}H and $^{31}P\{^1H\}$ NMR spectra and was considered to be complete after 24 h. The mixture was concentrated on a vacuum line and the residue recrystallized from hexanes to give **2e** (170.6 mg, 96%) as a deep orange solid: ^{1}H NMR (C_6D_6, 500 MHz) δ 8.75 (d, $J = 7.6$ Hz, 2 H), 7.87 (d, $J = 8.0$ Hz, 2 H), 7.42 (t, $J = 7.6$ Hz, 2 H), 7.32 (t, $J = 7.6$ Hz, 2 H), 7.11 (t, $J = 7.5$ Hz, 1 H), 7.01 (t, $J = 7.5$ Hz, 1 H), 2.26−2.34 (m, 6 H), 2.13 (br d, $J = 10$ Hz, 6 H), 2.06 (br d, $J = 10$ Hz, 6 H), 1.56−1.82 (m, 30 H), 1.06−1.28 ppm (m, 18 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 167.58 (dt, $^1J_{RhC} = 20.2$ Hz, $^2J_{PC} = 4.6$ Hz, O═*C*═C), 141.05, 138.46, 129.43, 128.72, 128.66, 128.49, 124.48, 124.29, 77.25 (d, $^1J_{RhC} = 3.0$ Hz, O═C═*C*), 32.54 (vt, $N = 17.9$ Hz, 6 C), 30.52 (6 C), 30.23 (6 C), 28.58 (vt, $N = 10.4$ Hz, 6 C), 28.55 (vt, $N = 9.4$ Hz, 6 C), 27.26 ppm (6 C); $^{31}P\{^1H\}$ NMR (C_6D_6, 80.95 MHz) δ 22.57 ppm (d, $^1J_{RhP} = 107.1$ Hz); IR (NaCl, C_6D_6) 1645, 1589, 1444 cm^{-1}. Anal. Calcd For $C_{50}H_{76}ClRhOP_2$ (893.16): C, 67.23; H, 8.59. Found: C, 67.16; H, 8.99.

***trans*-Chlorobis(triisopropylphosphine)(η^2-*C,O*-diphenylketene)iridium (2a):** ^{1}H NMR (C_6D_6, 300 MHz) δ 8.63 (d, $J = 7.2$ Hz, 2 H), 7.63 (d, $J = 7.2$ Hz, 2 H), 7.33 (t, $J = 7.6$ Hz, 2 H), 7.29 (t, $J = 8.0$ Hz, 2 H), 7.09 (app t, $J = 7.2$ Hz, 1 H), 7.03 (app t, $J = 7.1$ Hz, 1 H), 2.45 (m, 6 H, PC(*H*)CH$_3$CH$_3$), 1.19 (dvt, $J = 7.1$ Hz, $N = 14$ Hz, 18 H, PC(H)C*H*$_3$CH$_3$), 1.16 ppm (dvt, $J = 7.2$ Hz, $N = 14$ Hz, 18 H, PC(H)CH$_3$C*H*$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz) δ 143.78 (t, $J =$

3.2 Hz, O═*C*═C), 141.95 (ipso *C*), 138.60 (ipso *C*), 128.79, 128.76 [a tall peak with an intensity greater than two $C_{(sp^2)}H$ carbons], 128.58, 124.97 (para *C*), 123.93 (para *C*), 74.75 (O═C═*C*), 21.20 (vt, N = 24.6 Hz), 19.43, 18.96 ppm; $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ 20.90 ppm; IR (KBr) 1636, 1589, 1493 cm^{-1}. Anal. Calcd for $C_{32}H_{52}ClIrOP_2$ (742.45): C, 51.76; H, 7.07. Found: C, 51.95; H, 7.04.

***trans*-Chlorobis(tricyclohexylphosphine)(η^2-*C,O*-diphenylketene)iridium (2b).** Following the general procedure, [(μ-Cl)Ir(cyclooctene)$_2$]$_2$ (89.6 mg, 0.100 mmol) in C_6D_6 (~0.6 mL) was treated with Ph_2C═C═O (39.5 mg, 0.203 mmol), followed by $P(Cy)_3$ (115.1 mg, 0.410 mmol), whereupon a clear red solution formed. After 24 h, the mixture was concentrated on a vacuum line and the residue recrystallized from hexanes to give **2b** as dark orange solid (196.5 mg, 94%): ^1H NMR (C_6D_6, 500 MHz) δ 8.66 (d, J = 7.2 Hz, 2 H), 7.84 (d, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.6 Hz, 2 H), 7.33 (t, J = 7.8 Hz, 2 H), 7.14 (t, J = 7.8 Hz, 1 H), 7.07 (t, J = 7.8 Hz, 1 H), 2.35−2.45 (m, 6 H), 2.13 (br d, J = 11.5 Hz, 6 H), 2.02 (br d, J = 11.5 Hz, 6 H), 1.76 (br t, J = 9.8 Hz, 12 H), 1.63 (br dd, J = 2.5, 10.5 Hz, 18 H), 1.10−1.28 ppm (m, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 142.33 (t, J = 3.7 Hz, O═*C*═C), 141.17, 137.21, 128.81, 128.61, 127.68, 127.66, 123.41, 123.12, 74.42 (O═C═*C*), 31.04 (t, N = 23.9 Hz, 6 C), 29.84 (6 C), 29.44 (6 C), 28.10 (vt, N = 10.4 Hz, 12 C), 26.78 ppm (6 C); $^{31}P\{^1H\}$ NMR (C_6D_6, 80.95 MHz) δ 10.99 ppm; IR (NaCl, C_6D_6) 1627, 1591, 1441 cm^{-1}. Anal. Calcd for $C_{50}H_{76}ClIrOP_2$ (982.52): C, 61.12; H, 7.81. Found: C, 60.65; H, 8.08.

***trans*-Chlorobis(di-*tert*-butylmethylphosphine)(η^2-*C,O*-diphenylketene)iridium (2c).** Following the general procedure, to a suspension of [(μ-Cl)Ir(cyclooctene)$_2$]$_2$ (179.2 mg, 0.200 mmol) in C_6D_6 (~1.5 mL) was added Ph_2C═C═O (78.6 mg, 0.405 mmol), followed by $P(C_4H_9)_2(CH_3)$ (128.2 mg, 0.800 mmol). The resulting clear red solution was allowed to stand for 24 h before concentration and recrystallization from hexane to give **2c** (222.0 mg, 75%) as a deep red solid: ^1H NMR (C_6D_6, 500 MHz) δ 8.42 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.33 (t, J = 8.6 Hz, 2 H), 7.27 (t, J = 8.6 Hz, 2 H), 7.12 (t, J = 8.5 Hz, 1 H), 7.09 (t, J = 7.5 Hz, 1 H), 1.32 (vt, N = 12.5 Hz, 18 H), 1.26 (vt, N = 13.5 Hz, 18 H), 0.71 ppm (vt, N = 6.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 138.18 (t, J = 3.9 Hz, O═*C*═C), 140.25, 138.24, 128.23, 128.15, 127.88, 127.51, 124.56, 123.18, 76.01 (O═C═*C*), 35.78 (vt, N = 22.9 Hz, 2 C), 35.33 (vt, N = 23.3 Hz, 2 C), 30.67 (6 C), 30.22 (6 C), −2.43 ppm (vt, N = 25.5 Hz, 2 C); $^{31}P\{^1H\}$ NMR (C_6D_6, 80.95 MHz) δ 17.85 ppm; IR (NaCl, C_6D_6) 1624, 1591, 1471 cm^{-1}; FAB MS (*m/z*) 743 (15%), 742.282 00 (31%, calcd for $C_{32}H_{52}ClIrOP_2$, 742.281 14), 740 (15), 436 (21), 434 (12), 167 (22), 161 (100).

***trans*-Chlorobis(triisopropylphosphine)(η^2-*C,O*-diphenylketene)rhodium (2d).** In a slight modification of the general procedure, to a suspension of [(μ-Cl)Rh(cyclooctene)$_2$]$_2$ (38.6 mg, 0.0538 mmol) and C_6D_6 (~0.5 mL) was added P(*i*-Pr)$_3$ (37.5 mg, 0.234 mmol), followed 25 min later by Ph_2C═C═O (20.8 mg, 0.113 mmol). By ^1H and especially $^{31}P\{^1H\}$ NMR it required ~1 h for the ketene complex to be formed, but the clear red solution was allowed to react for 14 h before it was concentrated on the vacuum line and the residue crystallized from toluene−petroleum ether to give **2d** (49.0 mg, 70%) as a red solid: ^1H NMR (C_6D_6, 499.88 MHz) δ 8.76 (d, J = 7.5 Hz, 2 H), 7.65 (d, J = 7 Hz, 2 H), 7.37 (t, J = 7.5 Hz, 2 H), 7.27 (t, J = 7.5 Hz, 2 H), 7.07 (t, J = 7 Hz, 1 H), 7.02 (t, J = 7 Hz, 1 H), 2.27−2.39 (m, 6 H), 1.18 ppm (dvt, J = 6.5 Hz, N = 13.5 Hz, 36 H); $^{13}C\{^1H\}$ (C_6D_6, 125.7 MHz) δ 167.77 (dt, J_{RhC} = 20.1 Hz, J_{PC} = 5.6 Hz), 140.91 (1 C), 138.79 (1 C), 128.94 (2 CH), 128.92 (2 CH), 128.78 (2 CH), 128.71 (2 CH), 124.99 (1 CH), 124.28 (1 CH), 77.06 (d, $^1J_{RhC}$ = 2.1 Hz), 22.63 (vt, N = 18.9 Hz), 20.03, 19.75 ppm; $^{31}P\{^1H\}$ (C_6D_6, 202.3 MHz) δ 32.55 ppm (d, J = 112.0 Hz); IR (KBr) 2958 (m), 2928 (m), 2871 (m), 1656 (s), 1599 (m), 1590 (m), 1494 (m), 1461 (m), 1446 (m), 1431 (m), 1242 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{52}ClORhP_2$ (653.06): C, 58.85; H, 8.03. Found: C, 58.96; H, 8.29.

***trans*-Chlorobis(di-*tert*-butylmethylphosphine)(η^2-*C,O*-diphenylketene)rhodium (2f).** Following the general procedure, to a suspension of [(μ-Cl)Rh(cyclooctene)$_2$]$_2$ (72.2 mg, 0.101 mmol) and C_6D_6 (~1.0 mL) was added Ph_2C═C═O (39.0 mg, 0.243 mmol), followed by $P(C_4H_9)_2(CH)_3$ (73.0 mg, 0.456 mmol). The resulting clear red solution was allowed to react for 24 h before it was concentrated on the vacuum line and the residue crystallized from hexanes to give **2f** (99.5 mg, 76%) as a deep red solid: ^1H NMR (C_6D_6, 500 MHz) δ 8.57 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.2 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 2 H), 7.28 (t, J = 8.2 Hz, 2 H), 7.10 (m, 2 H), 1.35 (vt, N = 12.5 Hz, 18 H), 1.25 (vt, N = 13.5 Hz, 18 H), 0.70 ppm (vt, N = 5.0 Hz, 6 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz) δ 165.13 (dt, J_{RhC} = 20.7 Hz, J_{PC} = 5.8 Hz, O═*C*═C), 140.11, 139.22, 129.03, 128.97, 128.94, 128.44, 125.20, 124.37, 79.17 (d, $^1J_{RhC}$ = 2.3 Hz, O═C═*C*), 35.73 (vt, N =15.6 Hz, 2 C), 35.47 (vt, N = 17.8 Hz, 2 C), 30.50 (6 C), 30.40 (6 C), −0.59 ppm (t, J = 9.2 Hz, 2 C); $^{31}P\{^1H\}$ NMR (C_6D_6, 80.95 MHz) δ 31.97 ppm (d, J = 109.1 Hz); IR (NaCl, C_6D_6) 1650, 1594, 1475 cm^{-1}; FAB MS (*m/z*) 652.2268 (8%, calcd for $C_{32}H_{52}ClRhOP_2$, 652.2237), 460 (33), 459 (21), 458 (100), 161 (74).

***trans*-Chlorobis(triisopropylphosphine)(η^2-C,C-phenylketene)iridium (4):** ^1H NMR (C_6D_6, 300 MHz) δ 7.76 (d, J = 6.5 Hz, 2 H), 6.90−7.07 (m, 3 H), 3.51 [dd, J = 6.5, 11.1 Hz, 1 H, O═C═C(*H*)-(Ph)], 2.54 [octet of d, J = 7.2 ($^3J_{HH}$ = $^4J_{HP}$), 14.4 Hz ($^2J_{HP}$), 3 H, PC(*H*)(CH$_3$)$_2$], 2.26 (octet of d, J = 7.2 ($^3J_{HH}$ = $^4J_{HP}$), 14.4 Hz ($^2J_{HP}$), 3 H, PC(*H*)CH$_3$CH$_3$), 1.27−1.33 ppm (m, 36 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 198.41 (t, J = 2.9 Hz, O═*C*═C), 137.89 (dd, J = 2.1, 3.4 Hz, ipso *C*), 128.09, 125.49, 23.67 (dd, J = 4.3, 21.7 Hz), 23.22 (dd, J = 3.9, 21.6 Hz), 20.61, 20.57, 20.14, 19.92, −32.83 to −32.77 ppm (not well-resolved dd, two slightly broad lines (δ −32.80, −32.81 ppm) were observed with equal intensities, O═C═*C*), missing one aryl carbon; $^{31}P\{^1H\}$ NMR (C_6D_6, 202.3 MHz) δ 25.43 (d, J = 323.5 Hz), 23.30 ppm (d, J = 323.5 Hz); IR (KBr) 1763, 1460, 1248 cm^{-1}. Anal. Calcd for $C_{26}H_{48}ClIrOP_2$ (666.35): C, 46.86; H, 7.28. Found: C, 46.63; H, 6.90.

X-ray Diffraction Study on 2c. A red block measuring 0.42 × 0.40 × 0.52 mm^3 was mounted in an X-ray capillary and placed in a precooled N_2 stream at −100 °C using the Siemens LT 2a low-temperature device on a Siemens P4 autodiffractometer. Centering of 23 randomly selected reflections between 3.0 and 30.0° 2θ revealed a primitive orthorhombic cell. Data collection of $^1/_4$ of the hemisphere was completed, and an absorption correction was made using empirical ψ scan data. No appreciable deterioration of the check reflections occurred during data collection. Data reduction and analysis revealed the space group $Pna2_1$. Structure solution using Patterson methods revealed the position of the Ir, Cl, and P atoms, and the remaining non-hydrogen atoms were located by subsequent cycles of least-squares refinement, Fourier synthesis, and difference maps. Least-squares refinement led to a successful anisotropic convergence for all non-hydrogen atoms. The Siemens package of programs (SHELXTL PLUS) was used throughout for solution and refinement. Formula $C_{32}H_{52}ClIrOP_2$ (742.3), orthorhombic, space group $Pna2_1$, red color, a = 15.340(6) Å, b = 18.825(7) Å, c = 11.638(5) Å at 173 K, Z = 4, final R indices (observed data) R = 2.88%, wR = 3.52%, R indices (all data) R = 3.40%, wR = 3.93%, and GOF = 0.84.

X-ray Diffraction Study on 4. As for **2c**, a suitable specimen 0.08 × 0.25 × 0.55 mm in size was analyzed at −100 °C. The Siemens random search program located 25 reflections between 15 and 30° 2θ. Centering these reflections indicated a monoclinic primitive cell. Collection was conducted on $^1/_2$ of the hemisphere. Data reduction gave the unambiguous $P2_1/c$ space group (No. 14). Direct methods successfully located the Ir, Cl, and P atoms, and the remaining non-hydrogen atoms were located in subsequent difference maps and refined in least-squares cycles. Hydrogen atoms were assigned a riding model on the carbon atoms. The Siemens package of programs (P3, SHELXS, SHELXL) was used exclusively for the structure determination and refinement. Formula $C_{26}H_{48}ClIrOP_2$ (666.2), monoclinic, space group $P2_1/c$, yellow plate, a = 11.723(4) Å, b = 14.607(4) Å, c = 17.573(5) Å, β = 107.48(2)° at 173 K, Z = 4, final R indices (observed data) R = 4.04%, wR = 5.49%, R indices (all data) R = 6.22%, wR = 6.12%, and GOF = 1.28.

Phenylacetic Acid-1-^{13}C. Toluene (65 mL, 56 g, 0.61mol) was placed in a flask under N_2 atmosphere. *N,N′*-Tetramethylethylenediamine (TMEDA) (33 mL, 25.6 g, 220 mmol) and BuLi (80 mL of 2.5 M solution in hexane, 200 mmol) were added dropwise. The mixture was heated to a gentle reflux for 30 min. After cooling, THF (140 mL) was added and the mixture was transferred to a 500-mL flask containing $^{13}CO_2$ (22 mmol). After stirring overnight, the reaction mixture was quenched with water, and the resulting mixture was extracted twice with aqueous NaOH (1 M). To the combined aqueous layers was added aqueous HCl until the pH was less than 1, and the product was extracted with ether. The combined organic layers were dried with $MgSO_4$, and the solvent was removed. The remaining solid was purified via hot Soxhlet extraction with hexanes, to give 2.06 g (15 mmol, 67%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.69 (s, br, 1 H, O*H*), 7.30−7.33 and 7.25−7.27 (m, 5 H), 3.63 ppm (d, $J = 8$ Hz, 2 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 178.42 ($^{13}\mathit{C}$OOH), 133.43 (d, $J = 2$ Hz, ipso C), 129.57 (d, $J = 2$ Hz, 2 CH), 128.85 (2 CH), 127.56 (CH), 41.27 ppm (d, $J = 55$ Hz, CH_2) [satellites of *C*OOH peak: δ 178.40 ($^{13}C^{18}$OOH, 1.8% intensity), 178.42 ppm (d, $J = 55$ Hz, $Ph_2{}^{13}CH^{13}\mathit{C}OOH$, 1% intensity]; IR (KBr) 3063, 1661 ($^{13}C{=}O$), 1499, 1454, 1408, 1339, 1232, 1181, 919, 751, 700, 676, 604, 479 cm^{-1}.

Phenylacetic Acid-1-^{13}C Chloride. Phenylacetic-1-^{13}C acid (2.06 g, 15 mmol) was dissolved in $SOCl_2$ (10 mL), and the reaction mixture was heated to reflux for 1 h. Excess reagent was distilled off, and the residue was distilled under reduced pressure (∼10 Torr) to give the acid chloride as a clear pungent liquid (1.35 g, 8.7 mmol, 60%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.39 and 7.26−7.28 (m, 5 H), 4.14 ppm (d, $J = 8$ Hz, 2 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 172.02 ($^{13}\mathit{C}$OCl), 131.45 (d, $J = 4$ Hz, C), 129.68 (d, $J = 2$ Hz, 2 CH), 129.16 (2 CH), 128.32 (CH), 53.16 ppm (d, $J = 53$ Hz, $\mathit{C}H_2$).

4-(1-^{13}C). Phenylacetyl chloride-1-^{13}C (459.3 mg, 2.95 mmol) and dry Et_2O (10 mL) were stirred in an ice-cooled flask under nitrogen. Triethylamine (318.8 mg, 3.15 mmol) was added dropwise by syringe over 0.5 min. A thick white precipitate formed. The mixture was stirred for 5.5 h while the flask was cooled in ice. Meanwhile, 10 min before filtering the cold mixture containing acid chloride and base, to a separate flask containing a stirred suspension of $[(\mu\text{-Cl})Ir(cyclooctene)_2]_2$ (146.3 mg, 0.163 mmol) and dry benzene (3 mL) was added $P(i\text{-}Pr)_3$ (138.0 mg, 0.861 mmol) by syringe. An orange solution resulted. After 10 min under positive nitrogen pressure, a dry Schlenk filter was placed between the two flasks, and the cold ethereal mixture was quickly filtered into the benzene solution. The white filter cake was washed with by injecting a few milliliters of dry Et_2O through the Schlenk flask sidearm under positive nitrogen pressure. A yellow-orange solution resulted. As soon as filtration was complete, the reaction mixture was concentrated on the vacuum line and the residue was applied to a 1-mm SiO_2 plate on the Chromatotron, using ∼1 mL of benzene to rinse the flask before petroleum ether was applied as eluent. Once benzene was washed onto the plate, EtOAc−petroleum ether (1:40) was used to elute the plate. The desired ketene complex was the first colored band to come off the plate. A second purification was necessary to remove organic impurities. From two runs [using a total of 1.047 g of acid chloride, 325.3 mg of $[(\mu\text{-Cl})Ir(cyclooctene)_2]_2$, and 303.2 mg of $P(i\text{-}Pr)_3$], 6.3 mg of pure **4**-(1-^{13}C) and 26.0 mg of less pure sample were obtained (total yield, 5%): $^{13}C\{^{1}H\}$ (C_6D_6, 125.7 MHz) δ 197.20 (dd, $J = 2.8, 3.1$ Hz), 125.83, 24.14 (dd, $J = 4.2, 21.8$ Hz), 23.42 (dd, $J = 3.8, 21.8$ Hz), 21.02 (3 C), 20.76 (3 C), 20.29 (6 C), −32.70 ppm (dd, $^{1}J_{CC} = 45.7$ Hz, $^{2}J_{PC} = 2.1$ Hz) (it was not possible to unequivocally identify other peaks for aromatic C); $^{31}P\{^{1}H\}$ (C_6D_6, 80.95 MHz) δ 25.56 (dd, $^{2}J_{PP} = 325.3$ Hz, $^{2}J_{PC} = 3.0$ Hz), 23.41 ppm (dd, $^{2}J_{PP} = 325.3$ Hz, $^{2}J_{PC} = 3.0$ Hz).

Diphenylacetic Acid-1-^{13}C. To dry diphenylmethane (84.12 g, 512 mmol) was added TMEDA (21.23 g, 183 mmol), followed by BuLi (76 mL of 2.5 M solution in hexane, 190 mmol). The resulting red mixture was heated to reflux for 14 h. The cold solution was transferred into a 1-L flask containing $^{13}CO_2$ gas at 1 atm (44.6 mmol). The flask was placed into a shaker for 20 h, after which time the reaction mixture was quenched with water. The mixture was extracted with ether and the organic layer was washed two times with aqueous NaOH solution (1 M). To the combined aqueous layers was added aqueous HCl until the pH became less than 1. The product was extracted with ether. Combined organic layers were dried with $MgSO_4$, and the solvent was removed. The product was dissolved in CH_2Cl_2, $MgSO_4$ was added to the heterogeneous mixture. The drying reagent was filtered off and the solvent removed, leaving the acid as colorless solid (6.26 g, 29 mmol, 65%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.0 (br s, 1 H, O*H*), 7.18−7.33 (m, 10 H), 5.03 ppm (d, $J = 8$ Hz, 1 H); $^{13}C\ \{^{1}H\}$ NMR and DEPT ($CDCl_3$, 125.7 MHz) δ 179.11 ($^{13}\mathit{C}$OOH), 138.10 (d, $J = 2$ Hz, 2 C), 128.88 (d, $J = 2$ Hz, 4 CH), 128.85 (4 CH), 127.69 (d, $J = 0.5$ Hz, 2 CH), 57.25 ppm (d, $J = 55$ Hz, CH) [satellites of the *C*OOH peak: δ 178.79 ($Ph_2CH^{13}\mathit{C}^{18}O^{18}OH$, 0.36% intensity), 179.09 ($Ph_2CH^{13}\mathit{C}^{18}OOH$, 14% intensity), 179.10 ppm ($Ph_2CH^{13}CH^{13}\mathit{C}OOH$, $J = 55$ Hz, 1% intensity)]; IR (KBr) 3024, 2903, 2784, 2681, 1661, 1599, 1583, 1498, 1449, 1392, 1305, 1212, 1079, 1033, 933, 747, 727, 696, 636, 501 cm^{-1}; MS (*m*/*z*, %) 215 (3), 214 (3), 213 (M^+, 21), 169 (1), 168 (17), 167 (100), 165 (39), 163 (3), 153 (3), 152 (21), 141 (1), 139 (3), 128 (2), 115 (4), 91 (1), 89 (2), 83 (4), 82 (4), 77 (3), 76 (1), 65 (2), 63 (3), 62 (1), 51 (4), 50 (2). Anal. Calcd for $^{13}CC_{13}H_{12}O_2$: C, 78.86; H, 5.67. Found: C, 78.63; H, 5.57.

Diphenylacetic Acid-1-^{13}C Chloride. Diphenylacetic acid-1-^{13}C (1.00 g, 4.69 mmol) was dissolved in $SOCl_2$ (10 mL). The reaction mixture was heated to reflux for 1 h. Excess reagent was distilled off, and the residue was distilled at reduced pressure ($p < 1$ Torr), giving 1.050 g (97%) of product: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24−7.42 (m, 10 H), 5.44 ppm (d, $J = 10$ Hz, 1 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 173.69 ($^{13}\mathit{C}$OCl), 136.46 (d, $J = 2$ Hz, 2 C), 129.23 (4 CH), 128.95 (d, $J = 3$ Hz, 4 CH), 128.39 (2 CH), 68.88 ppm (d, $J = 52$ Hz, CH).

Diphenylketene-1-^{13}C. Diphenylacetic acid-1-^{13}C chloride (1.00 g, 4.32 mmol) was dissolved in dry ether (10 mL). Triethylamine (437 mg, 4.32 mmol) was added. After 1 h, the heterogeneous mixture was filtered. The ether was removed, and the residue was distilled at reduced pressure (<1 Torr) to give a yellow oil (586 mg, 70%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.40 and 7.19−7.25 ppm (m, 10 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 201.28 ($^{13}\mathit{C}$O), 132.72 (d, $J = 5$ Hz, 2 C), 129.45 (4 CH), 127.91 (d, $J = 3$ Hz, 4 CH), 126.41 (2 CH), 47.03 ppm (d, $J = 107$ Hz, $\mathit{C}{=}^{13}C{=}O$) [satellite to $^{13}\mathit{C}$O peak δ 201.22 ppm ($^{13}C^{18}O$, 7% intensity)]; IR (hexane, NaCl) 2046 (s), 2019 (w, $^{13}C{=}^{18}O$), 1600 (m), 1494 (m), 1074 (w), 1032 (w), 756 (m), 693 (m) cm^{-1}.

2a-(1-^{13}C). Diphenylketene-1-^{13}C (43.5 mg, 0.223 mmol), $P(i\text{-}Pr)_3$ (71.5 mg, 0.446 mmol), and $[(\mu\text{-Cl})Ir(cyclooctene)_2]_2$ (100 mg, 0.112 mmol) were dissolved in benzene (1 mL). The mixture was purified using radial chromatography (SiO_2, hexane/ethyl acetate 40:1) to give a red product (52.1 mg, 0.070 mmol, 63%): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 142.50 (t, $J = 4$ Hz, $^{13}\mathit{C}$O), 141.27 (d, $J = 5$ Hz, C), 137.77 (C), 128.37 (d, $J = 2$ Hz, 2 CH), 128.11 (2 CH), 127.81 (d, $J = 4$ Hz, 2 CH), 127.79 (2 CH), 124.35 (CH), 122.93 (CH), 73.97 (d, $J = 92.5$ Hz, $\mathit{C}{=}^{13}C{=}O$), 21.32 (vt, $N = 26$ Hz, 6 CH), 19.77 (6 CH_3), 19.30 ppm (6 CH_3); $^{31}P\{^{1}H\}$ NMR δ 20.72 ppm (d, $J = 2$ Hz); IR (KBr) 2958, 2927, 2870, 1610, 1582, 1568, 1494, 1443, 1386, 1367, 1243, 1060, 932, 884, 757, 693, 667, 651, 526 cm^{-1}; MS (*m*/*z*, %) 747 (0.1), 746 (0.2), 745 (0.2), 744 (1), 742 (0.4), 195 (23), 168 (13), 167 (22), 166 (24), 165 (59), 162 (10), 161 (100), 160 (40), 159 (24), 118 (39), 105 (13), 86 (13), 84 (14), 77 (16), 76 (48), 75 (25), 69 (11), 49 (17), 43 (50), 41 (34).

2d-(1-^{13}C). Using a similar procedure with Rh dimer (51.3 mg, 0.071 mmol), $P(i\text{-}Pr)_3$ (45.0 mg, 0.281 mmol) and $Ph_2C{=}^{13}C{=}O$ (31.8 mg, 0.164 mmol), labeled complex **2d**-(1-^{13}C) (86 mg, 95%) was obtained. Signals affected by the presence of the ^{13}C label: $^{13}C\{^{1}H\}$ (C_6D_6, 125.7 MHz) δ 167.76 (dt, $J = 19.9, 4.8$ Hz, $C{=}\mathit{C}{=}O$), 140.92 (d, $^{2}J_{CC} = 4.5$ Hz, ipso carbon of one phenyl ring), 77.05 ppm (dd, $^{1}J_{CC} = 93.0$ Hz, $^{1}J_{RhC} = 2.0$ Hz, $\mathit{C}{=}C{=}O$). $^{31}P\{^{1}H\}$ (C_6D_6, 80.95 MHz) δ 32.63 ppm (dd, $^{1}J_{RhP} = 107.9$ Hz, $^{2}J_{CP} = 4.5$ Hz); IR (C_6D_6) 1617 (s), 1587 (s), 1491 (m), 1452 (s), 1326 (s) cm^{-1}.

Diphenylacetic Acid-C(^{18}O)$_2$H. Sodium metal (25 mg, 1.09 mmol) was added to $H_2{}^{18}O$ (0.5 mL, 25 mmol) in ethylene glycol (2 mL, twice distilled under vacuum from sodium). Diphenylacetonitrile (193 mg, 1.00 mmol) was added, and the resulting mixture was heated at 150 °C for 17 h. To the cooled mixture was added aqueous HCl (0.2 M, 30 mL) and the solution was extracted with ether. The combined organic layers were dried with $MgSO_4$ and the solvent was removed, leaving the acid as white solid (205.7 mg, 0.96 mmol, 95%).

Diphenylacetic Acid-^{18}O Chloride and Diphenylketene-^{18}O. The procedure used to make ^{13}C-labeled material was followed starting with $Ph_2CHC^{18}O_2H$ (205.7 mg, 0.96 mmol) and $SOCl_2$, affording after vacuum distillation 235.7 mg (1.02 mmol, more than 106%) of $Ph_2CHC^{18}OCl$, which was then converted to $Ph_2C{=}C{=}^{18}O$ (142 mg, 0.72

mmol, 75%): IR (hexane, NaCl) C═O 2075 cm^{-1}. A second, smaller band was seen at 2102 cm^{-1}, suggesting incomplete ^{18}O incorporation. The ratio of integrated areas was 3.8 to 1.

2a-(^{18}O). Diphenylketene-^{18}O (50 mg, 0.255 mmol), P(*i*-Pr)$_3$ (82 mg, 0.511 mmol), and [(μ-Cl)Ir(cyclooctene)$_2$]$_2$ (107.5 mg, 0.12 mmol) were dissolved in benzene (1 mL). The mixture was purified using radial chromatography (SiO$_2$, hexane/ethyl acetate 40:1) to give a red product (65 mg, 0.087 mmol, 73%).

Labeled Ketene Complex 7-(1-^{13}C). Prepared using diphenylketene-1-^{13}C according to the reported procedure for the unlabeled material.[14] Data influenced by ^{13}C enrichment at C-1: ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz) δ 23.6 ppm (dd, $^2J_{PC}$ = 47.5 Hz, $^1J_{CC}$ = 44.3 Hz, O═^{13}C═*C*); IR (CH$_2$Cl$_2$) 1693 cm^{-1}.

Labeled Ketene Complex 8-(1-^{13}C). The compound was prepared using diphenylketene-1-^{13}C according to the reported procedure for the unlabeled material.[13] Data influenced by ^{13}C enrichment at C-1: ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$, 125.7 MHz, −50 °C) δ 22.33 ppm (d, $^1J_{CC}$ = 54.4 Hz); IR (C$_6$D$_6$, NaCl) 1755 (s), 1737 (m), 1597 (w), 1476 (m), 1446 (m) cm^{-1}; ^{31}P{^{1}H} (C$_6$D$_6$, 81.0 MHz, 30 °C) δ 59.47 ppm (dd, $^1J_{RhC}$ = 228.2, $^2J_{CP}$ = 4.0 Hz).

Normal Coordinate Mode Analyses. Experimental vibrational data were fit using a nonlinear least-squares fitting program that varied the primary force constants identified in the *F* matrix of the generalized valence force field (GVFF). The diphenylketene fragment was analyzed using the R$_2$CCO fragment where *R* is a point mass equal to a phenyl ring, using calculated bond lengths and bond angles.[38] Although this calculation neglects electronic coupling to the phenyl C═C stretching modes, it accurately reproduces the experimental vibrational frequencies, suggesting that coupling of ν(CO) to these modes is negligible. In addition, the energy of ν(CO) is unaffected by reasonable values of f_{CR}. This approximation was continued in the metal-containing fragments, [M(η^2-R$_2$CCO)], where M = Ir, Rh, and R = phenyl group point mass. The structural parameters used in the construction of the *G* matrixes were taken from crystal structure data. Because no low-energy vibrational data are currently available, the metal−ligand bond stretching force constants were held constant in each of the calculations. The M−C and M−O symmetry coordinates contribute less than 2% to ν(CO) and so reasonably[85] are included in the calculation for the sake of completeness, but no conclusions can be drawn as to the accuracy of this value.

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Supporting Information Available: Complete details of the X-ray diffraction studies on **2c** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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