is difficult to achieve.

Further surface-solution chemistry connections are seen in $Cp'_2Th(CH_3)_2/MgCl_2$ CO dosing experiments, which evidence irreversible migratory insertion processes, most likely of the type previously observed in solution. $Cp'_2Th(CH_3)_2/MgCl_2$ propylene chemistry is dominated by initial allylic C-H activation/methane elimination. Subsequent chemistry involves olefin insertion and oligomerization as well as η^3-allyl formation. All of these have been previously noted in f-element solution chemistry.

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Supplementary Material Available: Figures 3, 12, 13, 15, and 16 showing NMR spectra (6 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of Metallacycle–Carbene and -Bis(carbene) Complexes. A New Intramolecular Carbene–Carbene Coupling Process

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Abstract: Halide ion abstraction from the neutral iridiacyclopentadiene complexes, Ir(CR=CRCR=CR)$(PPh_3)_2$Cl (**1**, R = CO_2CH_3), and Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)(Cl) (**2**, R = CO_2CH_3), leads to high yields of the cationic complexes, Ir(CR=CRCR=CR)$(PPh_3)_2$(L)(L')$^+BF_4^-$ (**3**, L = CO, L' = H_2O; **4**, L = CO, L' = $NCCH_3$; **5**, L = L' = $NCCH_3$; and **6**, L = CO, L' = PMe_3). Reaction of complex **1** and 3-butyn-1-ol generates the first example of a metallacycle–carbene complex Ir(CR=CRCR=CR)$(PPh_3)_2$(Cl)[=C$(CH_2)_3$O] (**7**; 81%). Similarly, reaction of **3** or **4** and 3-butyn-1-ol leads to formation of the carbene complex Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[=C$(CH_2)_3$O]$^+BF_4^-$ (**8**; 96%). Reaction of **4** and 4-pentyn-2-ol gives a 95% yield of the substituted carbene complex Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[=C$(CH_2)_2$CHCH$_3$O]$^+BF_4^-$ (**9**). The acetonitrile analogues, Ir(CR=CRCR=CR)$(PPh_3)_2(NCCH_3)$[=C$(CH_2)_3$O]$^+BF_4^-$ (**10**) and Ir(CR=CRCR=CR)$(PPh_3)_2(NCCH_3)$[=C$(CH_2)_2$CHCH$_3$O]$^+BF_4^-$ (**11**), are also prepared in excellent yield. The bis(carbene) complex Ir(CR=CRCR=CR)$(PPh_3)_2$[=C$(CH_2)_3$O]$_2^+BF_4^-$ (**12**) is available in one step from **5** (87%). The mixed bis(carbene) complex Ir(CR=CRCR=CR)$(PPh_3)_2$[=C$(CH_2)_2$CHCH$_3$O][=C$(CH_2)_3$O]$^+BF_4^-$ (**13**) is prepared from **7** by sequential reaction with $AgBF_4$ and 4-pentyn-2-ol. Complex **8** crystallizes in space group *Cc*, with a = 12.723 (2) Å, b = 21.195 (4) Å, c = 18.432 (3) Å, β = 90.37 (1)°, V = 4970 (1) Å^3, Z = 4, $R(F)$ = 3.11%, and $R_w(F)$ = 3.76%. Complex **12** crystallizes in space group $P\bar{1}$, with a = 12.951 (2) Å, b = 13.371 (2) Å, c = 18.071 (4) Å, α = 78.42 (2)°, β = 79.27 (2)°, γ = 78.14 (1)°, V = 2966 (1) Å^3, Z = 2, $R(F)$ = 4.35%, $R_w(F)$ = 4.87%. Reaction of compounds **8** and **9** with pyridine gives the pyridinium-substituted acyl complexes Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[C(=O)$CH_2CH_2CH_2NC_5H_5$]$^+BF_4^-$ (**14**) and Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[C(=O)$CH_2CH_2CH(CH_3)NC_5H_5$]$^+BF_4^-$ (**17**). Methylamine and bis(oxacyclopentylidene) complex **12** give a nearly quantitative yield of the iridium hydride complex Ir(CR=CRCR=CR)$(PPh_3)_2(NH_2CH_3)$(H) (**19**), $CH_3NH_3^+BF_4^-$, and 2-(2(5*H*)-furanylidene)tetarhydrofuran (**20**; 92%). The mixed bis(carbene) complex **13** undergoes reaction with methylamine to give iridium hydride **19** and the carbene coupling products 2-(2(5*H*)-furanylidene)-5-methyltetrahydrofuran (**24**; 45%) and 2-(2(5-methyl)furanylidene)tetrahydrofuran (**25**; 55%). Iridium hydride **19** reacts with HCl to regenerate **1** and with HBF_4 in acetonitrile to regenerate the bis(carbene) precursor **5**. The mechanism of this novel carbene ligand coupling chemistry is discussed.

Introduction

Interest in the properties and reactivity of metal–carbene complexes has continued unabated since E. O. Fischer reported the first examples of this compound class over 20 years ago.[2] Current interest in this area stems from the role of metal carbenes in alkene metathesis,[3] alkene and alkyne polymerization,[4] and cyclopropanation chemistry,[5] and as intermediates in an impressive array of synthetic methodology.[6,7] In an effort to develop new

(1) (a) University of California, San Diego. (b) University of Delaware. (c) PRC Doering Fellow.

(2) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(3) (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 499. (c) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

(4) (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907, and references therein. (b) Katz, T. J.; Lee, S. J.; Shippel, M. A. *J. Mol. Cata.* **1980**, *8*, 219. (c) Schrock, R. R.; Freudenberger, J. H.; Listemann, M. L.; McCullough, L. G. *J. Mol. Catal.* **1985**, *28*, 1. (d) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

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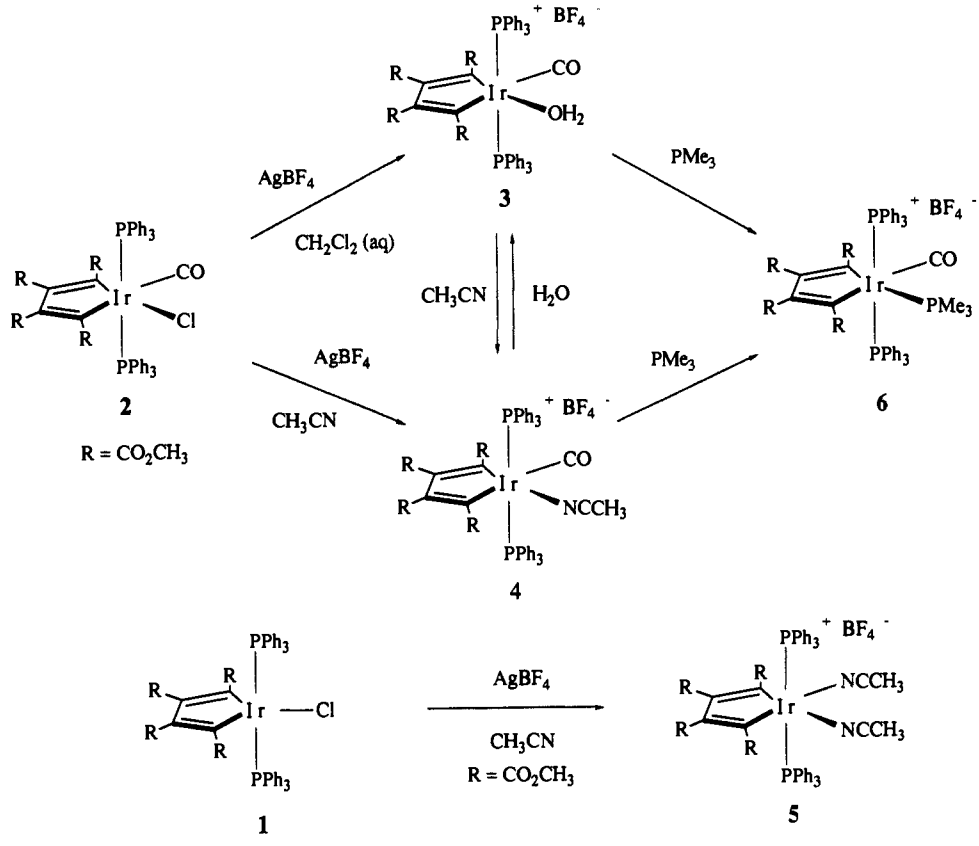
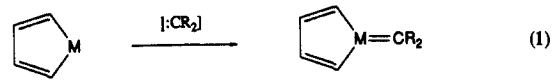
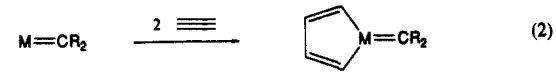
Scheme I. Synthesis of Cationic Iridiacyclopentadiene Complexes **3–6**



modes of metallacycle and carbene reactivity and to modify existing reactivity patterns, we recently initiated a research program centered around the synthesis, structure, and reactivity of metallacycle–carbene complexes.[8] Two potentially straightforward routes toward metallacycle–carbene complexes are introduction of a carbene ligand into an existing metallacycle complex (1), and



(1)



(2)

introduction of an η^2-1,4-buta-1,3-dienyl ligand into an existing carbene complex (2). Alkynes are convenient precursors to metallacycles; however, alkynes will also react with metal carbenes by addition across the metal–carbon double bond.[9] We therefore concentrated our initial efforts on the former synthetic route.[10] In this paper, we report full details on (a) the preparation and conversion of metallacyclopentadiene complexes to a new compound class—the metallacycle–carbenes; (b) the application of alkynol cyclization methodology to the synthesis of bis(carbene) complexes, including the first mixed bis(alkoxycarbene) complex; (c) the reactivity of the 2-oxacyclopentylidene ligand toward amines, including the remarkably facile ring-opening reaction of a 3-methyl-2-oxacyclopentylidene ligand, and the unprecedented amine-induced oxidative coupling of two oxacyclopentylidene ligands. Portions of this work have appeared in preliminary form.[8a-c,f]

Results

1. Synthesis and Characterization of Cationic Iridiacyclopentadiene Complexes 3–6. The cationic iridiacycle precursors to the desired carbene complexes were prepared directly from Collman's neutral iridium chloride metallacycles,[11] Ir(CR=CRCR=CR)$(PPh_3)_2$Cl (**1**, R = CO_2CH_3) and Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)(Cl) (**2**, R = CO_2CH_3), by halide ion abstraction (Scheme I). Addition of $AgBF_4$ (0.46 mmol) to a wet methylene chloride solution of **2** (0.41 mmol, 8

(5) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411, and references therein. (b) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (c) Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; p 135.

(6) (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1987; Vol. 1. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. Casey, C. P. *React. Intermed. (Wiley)* **1985**, *5*, 3. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (e) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689. (f) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (g) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. I. (h) Casey, C. P. *J. Organomet. Chem. Libr.* **1976**, *1*, 397. (i) Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407; **1972**, *30*, 353.

(7) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987; p 783.

(8) (a) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060. (c) O'Connor, J. M.; Pu, L.; Johnson, J. A.; Uhrhammer, R. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed., Kluwer Academic: Dordrecht, Holland, 1989; p 43. (d) O'Connor, J. M.; Pu, L.; Uhrhammer, R.; Johnson, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1889. (e) O'Connor, J. M.; Johnson, J. A. *Synlett* **1989**, *1*, 57. (f) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 4129.

(9) (a) Dötz, K. H. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Chapter 4. (b) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223. (c) Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717. (d) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(10) The cyclization of amino- and alkoxycarbenes with alkenes and alkynes has been reported to give five-membered carbocycles: (a) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070. (b) Grotjahn, D.; Dotz, K. H.; Horms, K. *Abstracts of Papers*; Fifth IUPAC Symposium on Organometallic Chemistry directed toward Organic Synthesis, Florence, Italy, October 1–6, 1989. (c) Harvey, D. F., personal communication.

(11) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298.

mM), followed by filtration and evaporation of the volatiles led to isolation of the cationic aquo complex, Ir(CR=CRCR=CR)$(PPh_3)_2(CO)(H_2O)^+BF_4^-$ (**3**), as a yellow solid in 70% yield. In a similar fashion treatment of **2** with $AgBF_4$ in acetonitrile solvent led to isolation of the acetonitrile analogue, Ir(CR=CRCR=CR)$(PPh_3)_2(CO)(NCCH_3)^+BF_4^-$ (**4**), as a off-white solid in 90% yield. When **4** (6.5×10^{-3} mmol, 15 mM) was dissolved in chloroform-d_1, which contained added water (9.5×10^{-3} mmol), an equilibrium with **3** was established over the course of 12 h at 23 °C, as determined by ^1H NMR spectroscopy ($K_{eq} = 4.2 \times 10^{-3}$).

Treatment of the coordinatively unsaturated metallacycle **1** with $AgBF_4$ led to formation of a cationic metallacycle containing two labile cis acetonitrile ligands, Ir(CR=CRCR=CR)$(PPh_3)_2(NCCH_3)_2^+BF_4^-$ (**5**), which was isolated as a yellow solid in 82% yield. In the workup of **5**, the initial product was recovered by filtration of the crude reaction mixture through Celite and evaporation of the solvent. Although, in solution, the product appeared pure by ^1H NMR spectroscopy, exposure to the air for long periods of time led to precipitation of a grey solid (presumably AgCl). Attempts at purification by repeated recrystallization met with limited success. It was ultimately found that removal of these salts was best achieved by gentle heating of an acetonitrile solution of the contaminated product in the air, followed by a second filtration through Celite to remove the grey silver halide precipitate.

The spectroscopic properties exhibited by the cationic metallacyclopentadiene complexes **3–5** are as follows. In the IR solution spectra, the carbonyl stretch was observed at 2070 cm^{-1} for the aquo complex **3** and at 2082 cm^{-1} for the acetonitrile analogue **4**; consistent with the moderate σ-donor and weak π-acceptor properties of the acetonitrile ligand. The IR stretching frequency of the methylcarboxylate ring substituents, ν(C=O), in **3–5**, also appeared sensitive to the degree of electron density at the metal center and was observed as a very broad band in the range 1690–1715 cm^{-1}. In the $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectra of **3–5**, a singlet was observed in the range −2 to −8 ppm, thereby requiring structures that contain a plane of symmetry. In the $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$) of **3** and **4**, the terminal carbonyl carbon resonance was observed at δ 173 (t, J = 8 Hz) and 169 (t, J = 8 Hz), respectively. The metallacycle carbons bonded directly to iridium were observed in the range δ 143–150 (t, J = 7–11 Hz) for **3** and **5**, whereas for **4**, these carbon resonances were assigned to triplets at 163 and 133 ppm. The observation of triplets ($\delta \sim 126$ (J = 56–59 Hz)) for the ipso carbons of the PPh_3 ligands is consistent with a trans relationship. The ortho and meta phenyl carbons of the PPh_3 ligands appeared as either triplets ($J_{PC+P'C} = \sim 10$ Hz) or broad resonances, also in the 125–145 ppm range. These resonances are readily distinguished from the metallacycle carbons on the basis of signal intensity. The small J_{PC} coupling constants (7–11 Hz) observed for the metallacycle carbons (Ir—C(R)=) were of a magnitude typical of a cis phosphorus–carbon relationship, which again requires trans PPh_3 ligands in **3–5**. For comparison, the closely related cobalt complex Co(CR=CRCR=CR)$(PMe_3)_2(NCCH_3)_2^+BPh_4^-$ (R = CO_2CH_3) was recently reported to exhibit a ^{13}C NMR chemical shift at 143.7 ppm for the metallacycle carbons bonded directly to cobalt.[12] In this particular case no coupling to phosphorus was observed and the structure was confirmed by X-ray crystallographic analysis.

In an effort to determine the effect of the trans ligand on the chemical shift of the metallacycle carbons, we prepared the PMe_3-substituted complex Ir(CR=CRCR=CR)$(PPh_3)_2(CO)(PMe_3)^+BF_4^-$ (**6**). Addition of excess PMe_3 to a chloroform solution of **4** at 23 °C (5 h) gave **6** as a pink solid in nearly quantitative yield. Surprisingly, in the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **6**, the metallacycle carbons bonded directly to iridium were both observed at 148 ppm; the carbon trans to the CO ligand as a triplet of doublets (J = 11, 6 Hz), and the carbon trans to the PMe_3 ligand as a doublet of triplets (J = 79, 9 Hz). The carbonyl carbon of **6** appeared as an unresolved multiplet at 173 ppm. In the IR spectrum of **6** a terminal carbonyl stretch was observed at 2053 cm^{-1}, as expected, the highest frequency ν(CO) stretch in the **3–6** series of complexes.

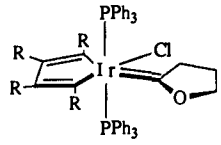
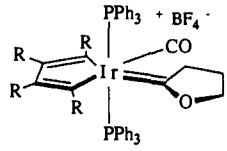
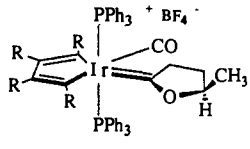
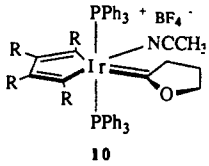
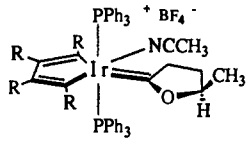
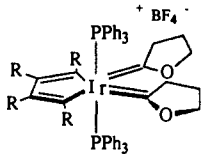
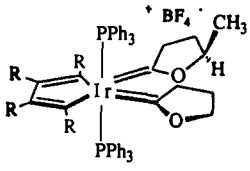
2. Synthesis and Characterization of Metallacyclopentadiene–Carbene Complexes 7–13. In order to avoid potential side reactions at the carbomethoxy metallacycle substituents we examined the reactivity of **1**, **3**, and **4** with the relatively non-nucleophilic carbene precursor 3-butyn-1-ol. Reaction of the unsaturated iridiacycle–halide complex Ir(CR=CRCR=CR)$(PPh_3)_2(Cl)$ (**1**; 15 mM) and 3-butyn-1-ol (19 mM) in chloroform at 23 °C (15 h) generated Ir(CR=CRCR=CR)$(PPh_3)_2(Cl)[=C(CH_2)_3O]$ (**7**) as a yellow solid in 88% isolated yield (Scheme II). Complex **7** represents the first example of an isolable metallacycle–carbene complex. The diagnostic spectroscopic properties exhibited by **7** are presented in Table I. The presence of the carbene ligand is confirmed by the observation of a triplet at 286.2 ppm (J = 6.2 Hz) in the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$). The ^1H NMR spectrum ($CDCl_3$) of **7** exhibited resonances assigned to the 2-oxacyclopentylidene ligand at δ 0.77 (p, J = 8.2 Hz, 2 H, Ir=CCH_2CH_2), 2.15 (t, J = 8.2 Hz, 2 H, Ir=CCH_2), and 4.30 (t, J = 8.3 Hz, 2 H, CH_2O). The equivalence of both hydrogens in each methylene unit requires that the plane of the oxacyclopentylidene ring be coincident with the plane of the metallacycle ring or that rapid rotation occurs about the iridium–carbene double bond on the NMR time scale. Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR (acetone-d_6) spectroscopy experiments indicated no significant line broadening of the methylene hydrogen or phosphorus resonances down to −85 °C. Thus, the carbene ligand remains in a static conformation or undergoes rapid rotation about the iridium–carbon bond even at −85 °C.

Cationic metallacycle–carbene complexes also proved to be readily accessible via 3-butyn-1-ol cyclization methodology. Thus, heating methylene chloride solutions of Ir(CR=CRCR=CR)$(PPh_3)_2(CO)(NCCH_3)^+BF_4^-$ (**4**; 0.49 mmol, 20 mM) and 3-butyn-1-ol (0.49 mmol) at reflux for 12 h led to nearly quantitative formation of the cationic carbene complex Ir(CR=CRCR=CR)$(PPh_3)_2(CO)[=C(CH_2)_3O]^+BF_4^-$ (**8**; 96%). Reaction of the aquo complex **3** (0.26 mmol, 5 mM) and 3-butyn-1-ol (0.40 mmol) in THF solution at 23 °C over the course of 12 h also generated **8** (75%). In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **8** the carbene carbon was observed as a broad signal due to unresolved J_{PC} coupling at 278.3 ppm and triplets were observed at δ 171 (J = 7 Hz), 161 (J = 11 Hz), and 140 (J = 10 Hz) for the three remaining carbon atoms bonded directly to iridium. The analogous ^{13}CO-labeled complex Ir(CR=CRCR=CR)$(PPh_3)_2(^{13}CO)[=C(CH_2)_3O]^+BF_4^-$ (**8**-^{13}CO) was prepared and a $^{13}C\{^1H\}$ NMR spectrum confirmed the 171 ppm resonance as that arising from the carbon atom of the CO ligand. In the ^1H NMR spectrum ($CDCl_3$) of **8** the carbene ligand hydrogens gave rise to signals at δ 1.59 (p, J = 8.0 Hz), 2.80 (t, J = 8.0 Hz, 2 H), and 4.74 (t, J = 8.3 Hz, 2 H). As was the case for **7**, the absence of diastereotopic methylene resonances for the carbene ligand requires either a plane of symmetry that includes both the carbene and metallacycle mean planes or rapid rotation about the iridium–carbon double bond on the NMR time scale. When an NMR sample of **8** (acetone-d_6) was subjected to a variable-temperature ^1H NMR study, there was no significant line broadening of the methylene hydrogen resonances between −85 and +85 °C.

Unexpectedly, when 4-pentyn-1-ol was added to a $CDCl_3$ solution of **4**, in an effort to generate a 2-oxacyclohexylidene analogue of **8**, no spectroscopic evidence was obtained to suggest

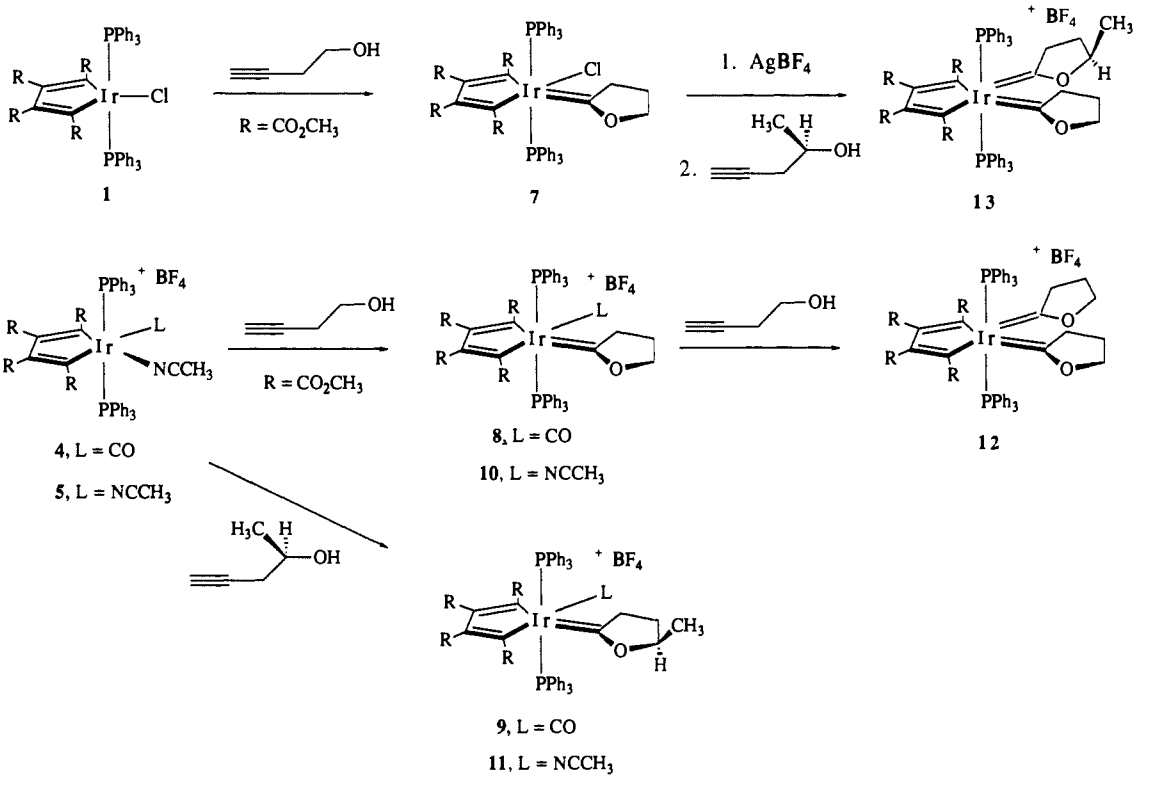
(12) Bouayad, A.; Dartiguenave, M.; Menu, M.-J.; Dartiguenave, Y.; Bélanger-Gariépy, F.; Beauchamp, A. L. *Organometallics* **1989**, *8*, 629.

Table I. Spectroscopic Characterization of Iridium-Carbene Complexes **7-12**

complex (R = CO_2CH_3)	^1H NMR,[a] δ	$^{13}C\{^1H\}$ NMR,[b] ppm	mass spectrum,[c] *m/e*
 **7**	0.77 (p, J = 8.2, 2 H, $CH_2CH_2CH_2$) 2.15 (t, J = 8.2, 2 H, $=CCH_2CH_2$) 3.21 (s, 3 H, CO_2CH_3) 3.42 (s, 3 H, CO_2CH_3) 3.46 (s, 3 H, CO_2CH_3) 3.60 (s, 3 H, CO_2CH_3) 4.30 (t, J = 8.3, 2 H, OCH_2CH_2) 7.2-7.7 (m, 30 H, 6 C_6H_5)	286.2 (t, J = 6.2, Ir=*C*) 152.4 (t, J = 6.8, Ir—*C*(R)=) 148.8 (t, J = 12.3, Ir—*C*(R)=)	1106 (M, 41) 1071 (M - Cl, 100) 1001 (M - Cl - C_4H_6O, 25) 844 (M- PPh_3, 63)
 **8**	1.59 (p, J = 8.1, 2 H, $CH_2CH_2CH_2$) 2.80 (t, J = 8.0, 2 H, $=CCH_2CH_2$) 3.23 (s, 3 H, CO_2CH_3) 3.39 (s, 3 H, CO_2CH_3) 3.47 (s, 3 H, CO_2CH_3) 3.52 (s, 3 H, CO_2CH_3) 4.74 (t, J = 8.3, 2 H, OCH_2CH_2) 7.4 (m, 30 H, 6 C_6H_5)	278.3 (br, Ir=C) 170.8 (t, J = 6.8, Ir—*C*O) 161.5 (t, J = 10.4, Ir—C(R)=) 140.3 (t, J = 10.0, Ir—C(R)=)	1099 (M - BF_4, 100) 1029 (M - BF_4 - C_4H_6O, 13) 1001 (M - BF_4 - C_4H_6O - CO, 19) 809 (M - BF_4 - PPh_3 - CO, 13)
 **9**	(C_6D_6) 1.08 (d, J = 6.3, 3 H, $CHCH_3$) 1.28 (p, J = 10.0, 1 H, CH_2CH_2CH) 2.28 (m, 1 H, CH_2CH_2CH) 2.84 (s, 3 H, CO_2CH_3) 3.11 (s, 3 H, CO_2CH_3) 3.41 (s, 3 H, CO_2CH_3) 3.42 (s, 3 H, CO_2CH_3) 3.67 (m, 2 H, $=CCH_2$) 5.22 (m, 1 H, OCH) 7.1-7.7 (m, 30 H, 6 C_6H_5)	278.0 (br)[d]	1113 (M - BF_4, 100) 1029 (M - BF_4 - C_5H_8O, 6) 1001 (M - BF_4 - C_5H_8O - CO, 13) 851 (M - BF_4 - PPh_3, 8) 821 (M - BF_4 - CO - $C_{12}H_{12}O_8$, 22)
 **10**	1.57 (p, J = 7.7, 2 H, $CH_2CH_2CH_2$) 2.12 (s, 3 H, $NCCH_3$) 3.05 (t, J = 7.8, $=CCH_2$) 3.32 (s, 6 H, 2 CO_2CH_3) 3.39 (s, 3 H, CO_2CH_3) 3.43 (s, 3 H, CO_2CH_3) 4.48 (t, J = 7.9, 2 H, OCH_2) 7.3-7.4 (m, 30 H, 6 C_6H_5)	285.2 (t, J = 6.4, Ir=C) 148.6 (t, J = 10.6) 147.7 (t, J = 7.5, Ir—*C*(R)=)	1112 (M - BF_4, 4) 1001 (M - BF_4 - C_4H_6O - $NCCH_3$, 100)
 **11**	1.18 (m, 2 H, CH_2CH_2CH) 1.41 (d, J = 6.3 Hz, 3 H, $CHCH_3$) 2.10 (s, 3 H, $NCCH_3$) 2.98 (m, 1 H, $=CCH_2$) 3.31 (m, 4 H, CO_2CH_3, $=CCH_2$) 3.33 (s, 3 H, CO_2CH_3) 3.44 (s, 3 H, CO_2CH_3) 3.58 (s, 3 H, CO_2CH_3) 4.36 (m, 1 H, $CHCH_3$) 7.3-7.5 (m, 30 H, 6 C_6H_5)	283.8 (t, J = 6.7, Ir=C) 150.4 (t, J = 10.8, Ir—C(R)=) 145.8 (m, Ir—*C*(R)=)	1085 (M - BF_4 - CH_3CN, 100) 1001 (M - BF_4 - CH_3CN - C_5H_8O, 20) 823 (M - BF_4 - CH_3CN - PPh_3, 74)
 **12**	(CD_3CN) 1.44 (p, J = 7.8, 4 H, $CH_2CH_2CH_2$) 2.69 (t, J = 7.8, 4 H, $=CCH_2$) 3.29 (s, 6 H, CO_2CH_3) 3.47 (s, 6 H, CO_2CH_3) 4.37 (t, J = 8.1, 4 H, OCH_2) 7.3-7.4 (m, 30 H, 6 C_6H_5)	(CD_3CN) 283.8 (t, J = 6.5, Ir=C) 153.7 (t, J = 9.9, Ir—C(R)=)	1141 (M - BF_4, 18) 1071 (M - BF_4 - C_4H_6O, 2) 1001 (M - BF_4 - 2(C_4H_6O), 3) 879 (M - BF_4 - PPh_3, 100)
 **13**	1.11 (p, br, J = 11.1, 2 H) 1.30 (d, J = 6.3, 3 H) 1.76 (m, 1 H) 1.87 (m, 1 H) 1.99 (m, 1 H) 2.41 (m, 1 H) 2.98 (m, 2 H) 3.32 (s, 3 H) 3.33 (s, 3 H) 3.34 (s, 3 H) 3.46 (s, 3 H) 4.55 (m, 1 H) 4.63 (q, J = 9, 1 H) 4.75 (br q, J = 9, 1 H) 7.32 (m, 3 H)	285.2 (t, J = 6.3, Ir=C=) 283.5 (t, J = 5.8, Ir=C=) 156.0 (m, Ir—C=) 150.2 (t, J = 9.8, Ir—C=)	1155 (M - BF_4, 16) 1001 (M - BF_4 - $C_9H_{14}O_2$, 4) 893 (M - BF_4 - PPh_3, 100)

[a] ^1H NMR spectra were recorded at 300 MHz in $CDCl_3$ (unless otherwise noted) at ambient probe temperature and were referenced to the residual solvent resonance at 7.24 ppm. All couplings are in hertz. [b] ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ (unless otherwise noted) at ambient probe temperature and were referenced to the solvent resonance at 77.0 ppm. All couplings are in hertz. [c] FAB mass spectra were obtained at the University of California, Riverside Mass Spectrometer Facility. [d] Carbene carbon coupling unresolved; unambiguous assignment of metallacycle carbons bound to iridium was not possible due to unresolved coupling.

Scheme II. Synthesis of Iridiacycle–Carbene Complexes **7–13**



formation of a carbene ligand. It was, however, possible to generate a substituted 2-oxacyclopentylidene ligand from 4-pentyn-2-ol and **4**. When a chloroform solution of **4** and excess 4-pentyn-2-ol was refluxed for 20 h a 95% yield of Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[=$C(CH_2)_2CHCH_3O$]$^+BF_4^-$ (**9**) was isolated following workup. In the ^1H NMR spectrum (C_6D_6) of **9** the carbene ligand hydrogens gave rise to resonances at δ 1.08 (d, J = 6.3 Hz, 3 H), 1.28 (p, J = 10.0 Hz, 1 H), 2.28 (m, 1 H), 3.67 (m, 2 H), and 5.22 (m, 1 H). Analogues of **8** and **9** that contain an acetonitrile ligand in place of the carbon monoxide ligand were readily accessible from the neutral carbene **7** or the bis(acetonitrile) complex **5**. Addition of $AgBF_4$ (1.4 mmol) to an acetonitrile solution of mono(carbene) **7** (0.90 mmol, 30 mM) led to isolation of Ir(CR=CRCR=CR)$(PPh_3)_2$-$(NCCH_3)$[=$C(CH_2)_3O$]$^+BF_4^-$ (**10**) as a yellow solid in 71% yield. An alternative preparation of **10** (in 94% yield) is via reaction of 3-butyn-1-ol (0.17 mmol) and bis(acetonitrile) complex **5** (0.146 mmol, 15 mM) at 23 °C (15 h). The 3-methyl-2-oxacyclopentylidene analogue Ir(CR=CRCR=CR)$(PPh_3)_2$-$(NCCH_3)$[=$C(CH_2)_2CHCH_3O$]$^+BF_4^-$ (**11**) was prepared in 91% yield by reaction of **5** (0.029 mmol, 88 mM) with 4-pentyn-2-ol (0.052 mmol) at 23 °C (24 h) in chloroform.

The observation that both neutral and cationic iridium complexes are converted to carbene complexes upon reaction with 3-butyn-1-ol led us to attempt the preparation of bis(carbene) complexes via alkynol cyclization chemistry. When chloroform solutions of mono(carbene) complex **10** and additional 3-butyn-1-ol were heated at reflux or allowed to stir at room temperature over extended periods of time, the bis(carbene) complex Ir(CR=CRCR=CR)$(PPh_3)_2$[=$C(CH_2)_3O$]$_2^+BF_4^-$ (**12**) was formed in high yield and isolated as a peach-colored solid. The most convenient preparative route to **12** is directly from **5** without isolation of the mono(carbene) intermediate **10**. Heating a chloroform solution of **5** (22 mM) and 3-butyn-1-ol (120 mM) at 50 °C for 3.5 h led to an 87% isolated yield of **12**. From the ^1H NMR spectrum (CD_3CN) the symmetrical nature of **12** is obvious. The resonances attributed to the carbene methylene hydrogens appear at δ 1.44 (p, J = 7.8 Hz, 4 H), 2.69 (t, J = 7.8 Hz, 4 H), and 4.37 (t, J = 8.1 Hz, 4 H). In the ^{13}C NMR spectrum only one downfield carbene carbon resonance is observed (δ 283.8 (t, J = 6.5 Hz)).

In an effort to apply alkynol cyclization methodology to the synthesis of mixed bis(carbene) complexes we examined the sequential conversion of 4-pentyn-2-ol and 3-butyn-1-ol to carbene ligands. Thus, the mixed bis(carbene) complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$[=$C(CH_2)_2CHCH_3O$][=$C(CH_2)_3O$]$^+BF_4^-$ (**13**) was conveniently prepared by addition of $AgBF_4$ (0.25 mmol) to a methylene chloride solution of oxacyclopentylidene complex **7** (0.069 mmol, 7.8 mM), followed by filtration of the resultant yellow-gray slurry and addition of 4-pentyn-2-ol (0.25 mmol). After ~16 h at room temperature, workup led to an 81% yield of **13**, isolated as a yellow solid. In the ^{13}C NMR spectrum of **13**, two downfield carbene carbon resonances were observed at δ 283.5 (t, J = 5.8 Hz) and 285.2 (t, J = 6.3 Hz). The magnitude of the phosphorus–carbon coupling constants requires trans triphenylphosphine ligands and therefore mutually cis carbene ligands.

3. X-ray Crystal Structure of Ir(CR=CRCR=CR)$(PPh_3)_2$-(CO)[=$C(CH_2)_3O$]$^+BF_4^-$ (8). X-ray data were acquired on a pale brown crystal of **8** obtained by slow evaporation of a chloroform/hexanes solution of **8** in the air (Table II). Refinement, described in the Experimental Section, gave the structure shown in Figure 1. Bond distances and bond angles are summarized in Table III. The 2-oxacyclopentylidene ligand conformation is consistent with that deduced from the spectroscopic data; the plane of the carbene ring bisects the plane of the metallacycle at an angle of 24°. The complex deviates from ideal octahedral geometry with the C(2)–Ir–C(5) angle constrained by the metallacycle ring to 77.4 (3)°. The iridium to metallacycle–carbon bond distances are 2.108 (7) and 2.101 (7) Å. These distances can be compared with the Ir to (sp^2) carbon distance of 2.104 (4) Å found in the metallacyclobutene complex *fac*-IrBr[CH_2C(*p*-tol)=C(*p*-tol)]$(PMe_3)_3$.[13,14] The carbon–carbon bond lengths

(13) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283.

Table II. Crystal and Data Collection, Refinement Parameters for **8** and **12**

	8	**12**
formula	$C_{53}H_{48}IrO_{10}P_2BF_4$	$C_{56}H_{54}O_{10}P_2IrBF_4 \cdot CHCl_3$
lattice type	monoclinic	triclinic
space group	*Cc*	$P\bar{1}$
a, Å	12.723 (2)	12.951 (2)
b, Å	21.195 (4)	13.371 (2)
c, Å	18.432 (3)	18.071 (4)
α, deg		78.42 (2)
β, deg	90.37 (1)	79.27 (2)
γ, deg		78.14 (1)
V, Å^3	4970 (1)	2966 (1)
Z	4	2
d_{calcd}, g cm^{-3}	1.585	1.509
μ, cm^{-1}	29.8	26.4
cryst dimens, mm	0.30 × 0.31 × 0.34	0.27 × 0.31 × 0.36
collectn temp, °C	23	20
radiation type	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range, deg	4–52	4–50
no. of reflcns read	5178	10702
no. of unique reflcns	5041	10346
no. of unique reflcns obsd	4748 ≥ 3$\sigma(F_o)$	7383 ≥ 3$\sigma(F_o)$
R_{int}, %	3.11	1.65
$R(F)$, %	3.47	4.35
$R_w(F)$ %	3.76	4.87
GOF	1.018	1.073
data/parameters	8.3	11.7
$\Delta\rho_{max}$, e Å^{-3}	1.8	1.49
structure soln	Patterson	Patterson
absorption correct	empirical	empirical
T_{max}/T_{min}	0.370/0.324	0.171/0.143

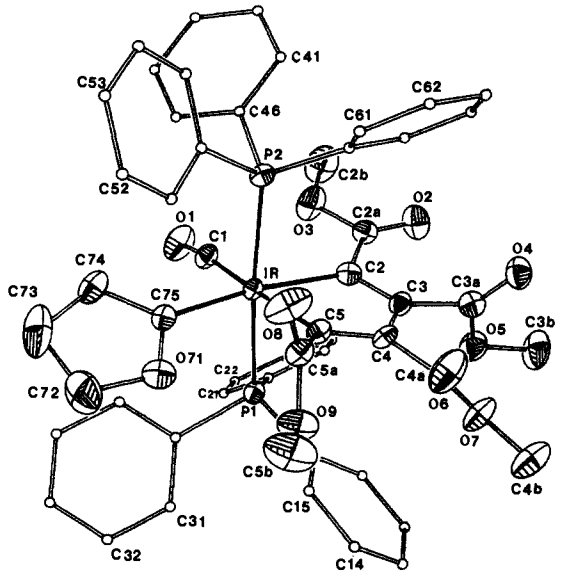


Figure 1. Structure of the cationic mono(carbene) complex Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[=C$(CH_2)_3$O]$^+BF_4^-$ (**8**); BF_4^- counterion omitted.

in the metallacycle ring are consistent with the presence of a conjugated 1,3-diene system: C(2)–C(3), 1.33 (1) Å; C(3)–C(4), 1.48 (1) Å; and C(4)–C(5), 1.33 (1) Å. The iridium to carbene carbon distance of 2.025 (7) Å is consistent with a metal–carbon double bond.[15] This distance can be compared to the closely related Ir–acyl carbon bond in Ir(CR=CRCR=CR)$(PPh_3)_2$(CO)[C(=O)$CH_2CH_2CH_2NC_5H_5$]$^+BF_4^-$ (**14**) (vide infra), which is 2.136 (4) Å. The C(75)–O(71) distance of 1.332 (9) in **8** compares to the acyl carbon–oxygen distance of 1.212 (5) Å in **14**.[8b]

(14) For Ir(III)–carbon bond distances, see: Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237, and references therein.

(15) For structurally characterized iridium carbene complexes, see: (a) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (b) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1982**, *236*, C7. (c) Bombieri, G.; Faraone, F.; Bruno, G.; Faraone, G. *J. Organomet. Chem.* **1980**, *188*, 379.

Table III. Selected Bond Distances and Angles for **8**

Bond Distances, Å

A	*B*	distance	*A*	*B*	distance
Ir	P(1)	2.445 (2)	O(71)	C(72)	1.461 (13)
Ir	P(2)	2.403 (2)	O(71)	C(75)	1.332 (9)
Ir	C(1)	1.925 (8)	C(72)	C(73)	1.498 (20)
Ir	C(2)	2.108 (7)	C(73)	C(74)	1.539 (16)
Ir	C(5)	2.101 (7)	C(74)	C(75)	1.470 (11)
Ir	C(75)	2.025 (7)	C(2)	C(2A)	1.499 (10)
O(1)	C(1)	1.143 (10)	C(3)	C(3A)	1.512 (10)
C(2)	C(3)	1.334 (10)	C(4)	C(4A)	1.498 (11)
C(3)	C(4)	1.483 (10)	C(5)	C(5A)	1.498 (10)
C(4)	C(5)	1.325 (10)			

Bond Angles, deg

A	*B*	*C*	angle	*A*	*B*	*C*	angle
P(1)	Ir	P(2)	172.6 (1)	C(5)	Ir	C(75)	94.8 (3)
P(1)	Ir	C(1)	84.7 (2)	Ir	C(1)	O(1)	174.5 (7)
P(2)	Ir	C(1)	92.8 (2)	Ir	C(2)	C(3)	114.9 (5)
P(1)	Ir	C(2)	85.0 (2)	C(2)	C(3)	C(4)	115.3 (6)
P(2)	Ir	C(2)	88.4 (2)	C(3)	C(4)	C(5)	115.9 (6)
C(1)	Ir	C(2)	96.1 (3)	Ir	C(5)	C(4)	115.2 (5)
P(1)	Ir	C(5)	91.5 (2)	C(72)	O(71)	C(75)	113.8 (7)
P(2)	Ir	C(5)	90.3 (2)	O(71)	C(72)	C(73)	106.5 (9)
C(1)	Ir	C(5)	172.7 (3)	C(72)	C(73)	C(74)	103.1 (10)
C(2)	Ir	C(5)	77.4 (3)	C(73)	C(74)	C(75)	108.2 (8)
P(1)	Ir	C(75)	91.6 (2)	Ir	C(75)	O(71)	121.0 (5)
P(2)	Ir	C(75)	95.4 (2)	Ir	C(75)	C(74)	130.9 (5)
C(1)	Ir	C(75)	91.5 (3)	O(71)	C(75)	C(74)	108.0 (6)
C(2)	Ir	C(75)	171.3 (3)				

Table IV. Selected Bond Distances and Angles for **12**

Bond Distances, Å

A	*B*	distance	*A*	*B*	distance
Ir	P(1)	2.427 (2)	O(10)	C(17)	1.288 (12)
Ir	P(2)	2.423 (2)	O(10)	C(20)	1.525 (12)
Ir	C(1)	2.146 (7)	C(1)	C(2)	1.341 (9)
Ir	C(4)	2.122 (6)	C(2)	C(3)	1.455 (11)
Ir	C(13)	2.033 (8)	C(3)	C(4)	1.349 (10)
Ir	C(17)	2.059 (7)	C(13)	C(14)	1.507 (14)
O(9)	C(13)	1.306 (9)	C(14)	C(15)	1.507 (14)
O(9)	C(16)	1.458 (13)	C(15)	C(16)	1.501 (17)
C(4)	C(8)	1.492 (11)	C(17)	C(18)	1.423 (11)
C(3)	C(7)	1.494 (9)	C(18)	C(19)	1.530 (15)
C(2)	C(6)	1.501 (11)	C(19)	C(20)	1.490 (17)
C(1)	C(5)	1.472 (12)			

Bond Angles, deg

A	*B*	*C*	angle	*A*	*B*	*C*	angle
P(1)	Ir	P(2)	175.3 (1)	Ir	C(1)	C(2)	113.9 (6)
P(1)	Ir	C(1)	89.0 (2)	C(1)	C(2)	C(3)	117.3 (7)
P(2)	Ir	C(1)	88.2 (2)	C(2)	C(3)	C(4)	116.4 (6)
P(1)	Ir	C(4)	86.7 (2)	Ir	C(4)	C(3)	114.9 (5)
P(2)	Ir	C(4)	89.0 (2)	Ir	C(13)	O(9)	119.2 (7)
C(1)	Ir	C(4)	77.4 (3)	Ir	C(13)	C(14)	133.1 (5)
P(1)	Ir	C(13)	93.7 (2)	O(9)	C(13)	C(14)	107.5 (7)
P(2)	Ir	C(13)	88.8 (2)	C(13)	C(14)	C(15)	105.4 (8)
C(1)	Ir	C(13)	174.9 (3)	C(14)	C(15)	C(16)	104.4 (10)
C(4)	Ir	C(13)	98.4 (3)	O(9)	C(16)	C(15)	103.7 (8)
P(1)	Ir	C(17)	89.3 (2)	Ir	C(17)	O(10)	120.0 (5)
P(2)	Ir	C(17)	94.7 (2)	Ir	C(17)	C(18)	129.3 (7)
C(1)	Ir	C(17)	94.0 (3)	O(10)	C(17)	C(18)	110.6 (7)
C(4)	Ir	C(17)	170.6 (3)	C(17)	C(18)	C(19)	107.3 (8)
C(13)	Ir	C(17)	90.4 (3)	C(18)	C(19)	C(20)	103.4 (8)
C(13)	O(9)	C(16)	115.0 (8)	O(10)	C(20)	C(19)	102.8 (9)
C(17)	O(10)	C(20)	112.4 (7)				

4. X-ray Crystal Structure of Ir(CR=CRCR=CR)$(PPh_3)_2$[=C$(CH_2)_3$O]$_2^+BF_4^-$ (12). X-ray data were acquired on a

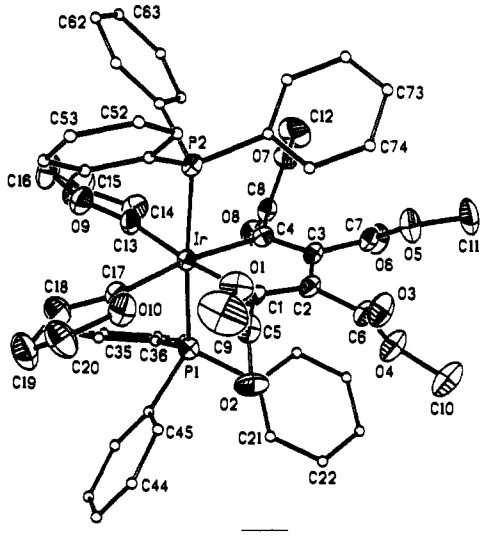
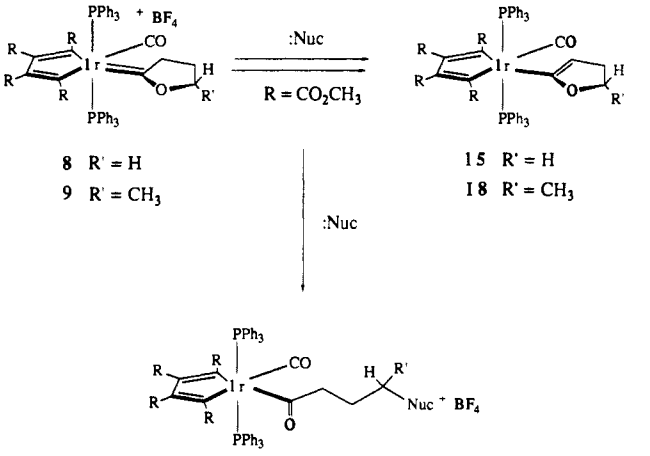


Figure 2. Structure of the cationic bis(carbene) complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$[=C(CH$_2$)$_3$O]$_2$$^+BF_4$$^-$ (**12**); BF$_4$$^-$ counterion omitted.

pale-brown crystal of **12** obtained by slow evaporation of a chloroform/hexanes solution of **12** in the air (Table II). Refinement, described in the Experimental Section, gave the structure shown in Figure 2. Bond distances and bond angles are summarized in Table IV. The 2-oxacyclopentylidene ligands in **12** are skewed such that the plane of the metallacycle bisects the plane of one carbene ring (C(13)–C(16), O(9)) at an angle of 29.4° and the second carbene ring at an angle of 31.5°. The oxygen atoms of both carbene ligands are situated on the same side of the plane defined by the metallacycle carbons. The iridium to carbene carbon distances are Ir–C(13), 2.033 (8) Å and Ir–C(17), 2.059 (7) Å; similar to that observed in **8**. It is interesting to note that the 2.059-Å distance for the iridium–carbene carbon distance is nearly identical with the iridium–vinyl carbon distance reported for (η^5-C$_5$Me$_5$)Ir(PMe$_3$)(H)(CH=CH$_2$).[16] In **12** the C(13)–O(9) distance is 1.306 (9) Å and the C(17)–O(10) distance is 1.288 (12) Å. The complex deviates from octahedral geometry with the C(1)–Ir–C(4) angle constrained by the metallacycle ring to 77.4°. As was observed for **8** the metallacycle ring carbons in **12** exhibit two short and one long carbon–carbon bond distance, consistent with the presence of a conjugated 1,3- diene system. There is little evidence for increased steric congestion in the coordination plane, which contains the carbene ligands and the metallacycle ring, in going from **8** to **12**. The C(17)–Ir–C(13) angle in **12** is 90.4 (3)° whereas the C(75)–Ir–C(1) angle in **8** is 91.5 (3)°.

5. Reactions of Cationic Carbenes 8 and 9 with Nucleophiles. When a methylene chloride solution of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[=C(CH$_2$)$_3$O]$^+$BF$_4$$^-$ (**8**; 0.13 mmol, 51 mM) and excess pyridine (2.5 mmol) was stirred for 12 h, a slow conversion to the pyridinium-substituted acyl complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(=O)CH$_2$CH$_2$CH$_2$NC$_5$H$_5$]$^+$BF$_4$$^-$ (**14**) occurred (Scheme III). Complex **14** was isolated as a yellow solid in 99% yield by evaporation of volatiles from the reaction mixture and trituration of the oil with hexanes. The IR spectrum of **14** exhibited a medium intensity band at 1630 cm^{-1}, which we attribute to overlapping ν(C=O) and pyridinium bands. In the ^{13}C{^{1}H} NMR spectrum (CDCl$_3$) of **14** a triplet was observed at δ 229.1 (J = 6.8 Hz), which is assigned to the acyl carbonyl carbon (Ir(*C*=O) CH$_2$). The structure of **14** was confirmed by X-ray crystallographic analysis.[8b] When the reaction of **8** and pyridine was monitored by ^{1}H NMR spectroscopy, resonances for an additional species were observed, which we attribute to formation of the neutral vinyl ether complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C=CH(CH$_2$)$_2$O] (**15**). This assignment was confirmed by independent synthesis of **15** from **8** and PMe$_3$ in CHCl$_3$ solution at 23 °C. In the ^{1}H NMR spectrum (CD$_2$Cl$_2$) of **15**, resonances assigned to the vinyl ether ligand were observed at δ 4.39 (s, br, 1 H, IrC=C*H*), 3.87 (t, J = 9.5 Hz, 2 H, C*H*$_2$O), and 2.36 (t, br, J = 9.4 Hz, 2 H, C*H*$_2$CH$_2$O). When **15** was treated with C$_5$H$_5$NH$^+$BF$_4$$^-$ in CD$_3$CN solution, ^{1}H NMR spectroscopy on the sample revealed rapid conversion to **8**, followed by slow conversion to acyl **14**. Triphenylphosphine was unreactive toward **8** under similar conditions; however, when **8** (0.031 mmol, 60 mM) and PPh$_3$ (0.06 mmol) were heated at 49 °C for ~35 h, the triphenylphosphonium-substituted acyl complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(=O)CH$_2$CH$_2$CH$_2$PPh$_3$]$^+$BF$_4$$^-$ (**16**) was formed in 87% yield. Isolated **16** exhibited an acyl stretch in the IR spectrum at 1622 (m) cm^{-1}. In the ^{13}C{^{1}H} NMR spectrum of **16** the acyl carbon was observed at δ 232 (t, J = 6.8 Hz). In the case of P(OMe)$_3$, no reaction with **8** was observed by ^{1}H NMR spectroscopy, even at 50 °C over the course of days.

Scheme III. Reactions of Cationic Carbenes **8** and **9** with Nucleophiles



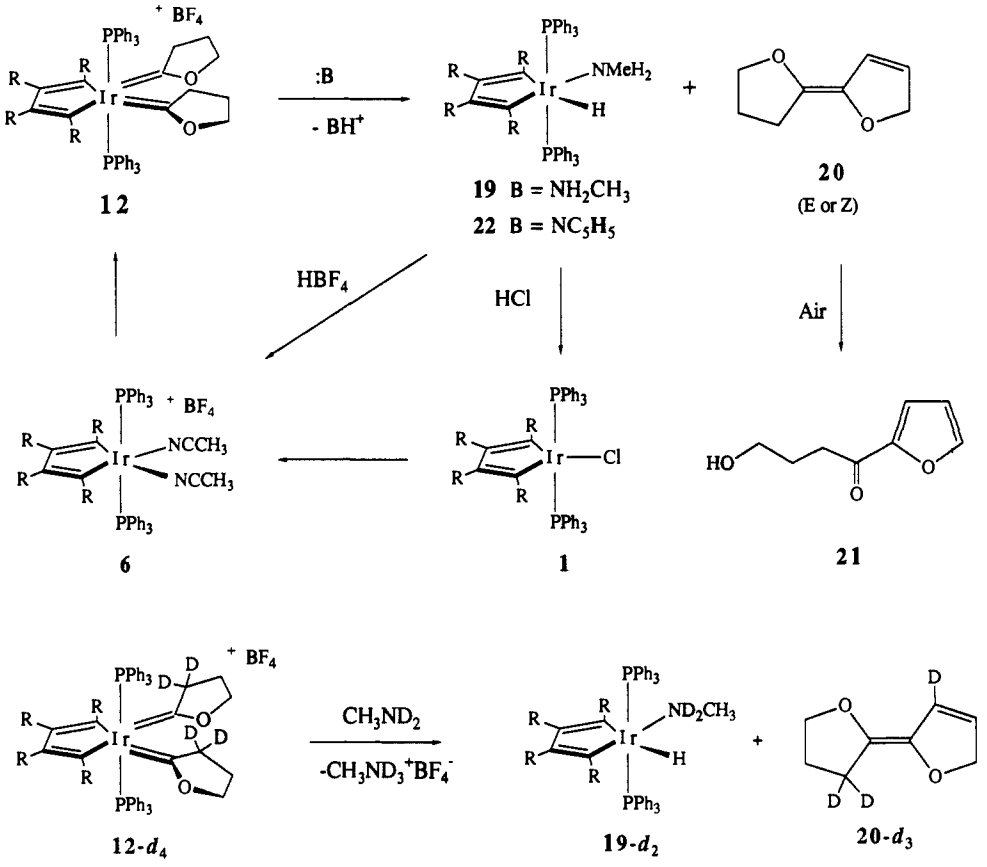
14 R' = H, Nuc = NC$_5$H$_5$
16 R' = H, Nuc = PPh$_3$
17 R' = CH$_3$, Nuc = NC$_5$H$_5$

The relatively mild conditions for conversion of **8** to **14** led us to explore the scope of the reaction by employing a carbene ligand with a secondary carbon center at the reactive carbon–oxygen bond. The 3-methyl-2-oxacyclopentylidene complex **9** underwent reaction with pyridine in CDCl$_3$ at 23 °C to give an equilibrium mixture of **9** and the neutral vinyl ether complex **18** (K_{eq} = 9.4 × 10^{-3}). Complex **18** was isolated in nearly quantitative yield by reaction of **9** and pyridine in C$_6$H$_6$ solvent. In this case, the **9** to **18** equilibrium was driven to the side of **18** by precipitation of C$_5$H$_5$NH$^+$BF$_4$$^-$ under the reaction conditions. Remarkably, when a chloroform solution of **9** (0.14 mmol, 10 mM) and pyridine (12.4 mmol) was heated at reflux, the pyridinium-substituted acyl complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(=O)-CH$_2$CH$_2$CH(CH$_3$)NC$_5$H$_5$]$^+$BF$_4$$^-$ (**17**) was generated in 63% yield. When imidazole was employed as the base in reactions with **9**, the vinyl ether complex **18** was formed, with no evidence for conversion to an acyl analogue of **17**.

6. Reactivity of Bis(carbene) Complex 12 toward Amines. Condensation of methylamine gas (34.7 mmol) into a yellow chloroform-d_1 solution of bis(oxacyclopentylidene) complex **12** (0.88 mmol, 88 mM) at −78 °C, followed by warming to 23 °C, resulted in rapid, nearly quantitative conversion to the iridium hydride complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(NH$_2$CH$_3$)(H) (**19**; 0.87 mmol), CH$_3$NH$_3$$^+BF_4$$^-$ (0.85 mmol), and 2-(2(5*H*)-furanylidene)tetrahydrofuran, (**20**; 0.81 mmol, 92% yield, Scheme IV). In the ^{1}H NMR spectrum (CDCl$_3$) of **19**, the hydride

(16) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

Scheme IV. Reaction of Bis(carbene) Complex **12** with Methylamine and Pyridine



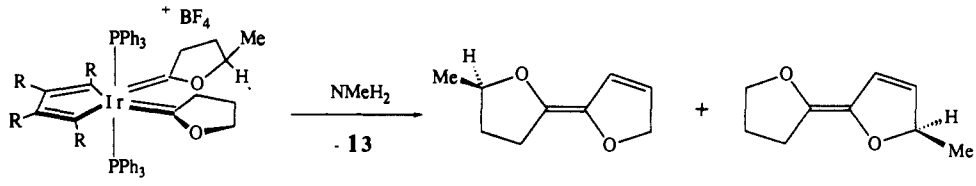
resonance was observed as a triplet at δ −10.6 (J_{PH} = 11 Hz, 1 H) whereas the amine ligand hydrogen resonances appeared as a triplet at δ 1.29 (J = 13 Hz, 3 H) and a broad resonance at δ 1.71 (2 H). In the IR spectrum of **19**, the Ir–H stretch appeared as a medium-intensity band at 2030 cm^{-1}. The carbene ligand coupling product **20** was characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy as well as mass spectroscopy and oxidation chemistry. The carbon resonances of the tetrasubstituted alkene were observed in the ^{13}C NMR spectrum at 140.3 and 133.4 ppm, as poorly resolved multiplets due to two bond and longer hydrogen couplings. The disubstituted alkene carbons appeared as doublets of multiplets at 122.1 and 124.4 ppm with $^1J_{CH}$ = 174 Hz. The observation of a pentet at δ 2.01 (J = 7 Hz, 2 H) in the ^1H NMR spectrum ($CDCl_3$) of **20** requires a $CH_2CH_2CH_2$ fragment in one ring, and a five-line pattern at δ 4.93 (J = 2 Hz, 2 H) is assigned to the allylic hydrogens of the methylene carbon bonded directly to oxygen. This five-line pattern is a consequence of a $^6J_{HH}$ = 2 Hz coupling to the methylene hydrogens at C(3) in the tetrahydrofuran ring, as well as ^4J and ^3J couplings of ~2 Hz. Saturation of the C(3) hydrogen resonance at 2.62 ppm resulted in collapse of the 4.93 ppm pentet to an apparent triplet (J = 2.1 Hz); the remaining splitting due to ~2 Hz coupling to both of the vinyl hydrogens ($^3J_{HH}$ = $^4J_{HH}$ = 2 Hz). When the 4.93 ppm resonance was saturated, the 2.62 ppm resonance became a broad triplet (J = 7.5 Hz), the 5.85 ppm multiplet (OCH_2CH=CH) became a broad doublet (J = 6 Hz), and the 6.43 ppm doublet of triplets became a doublet (J = 6 Hz). The spectroscopic data do not allow assignment of the alkene geometry as *E* or *Z*. We favor the *E* isomer on the basis of negligible NOE enhancement of the 2.62 ppm methylene resonance when the vinyl hydrogen resonance at 6.43 ppm was irradiated.

Consistent with the structural assignment for **20** was the observation that exposure of chloroform solutions of **20** to the air for 6.5 h at 23 °C resulted in conversion to furan **21** in 64% yield. The structure of **21** was readily assigned on the basis of spectroscopic data. In the ^1H NMR spectrum ($CDCl_3$) of **21** the three vinyl hydrogens were observed at δ 6.52 (dd, J = 4, 1 Hz, 1 H), 7.19 (d, J = 4 Hz, 1 H), and 7.56 (br, 1 H). In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) the acyl carbonyl carbon was assigned to a resonance at 189.6 ppm.

When pyridine was employed as the base in reactions with bis(carbene) **12** at 23 °C, the rate of reaction was much slower than in the case of methylamine. Reaction of **12** (0.005 mmol) and pyridine (0.025 mmol) in nitrobenzene-d_5 at 55 °C resulted in slow conversion (20 h) to **20** (46%) and Ir(CR=CRCR=CR)$(PPh_3)_2(NC_5H_5)$(H) (**22**; 46%), as determined by ^1H NMR spectroscopy. The pyridine adduct **22** was independently synthesized and isolated in 90% yield from a preparative-scale reaction of iridium hydride **19** (0.21 mmol, 35 mM) and excess pyridine (5 mmol) at 23 °C (3 days). In the ^1H NMR spectrum ($CDCl_3$) of **22** the hydride resonance was observed at δ −10.46 (t, J = 16 Hz, 1 H) and in the IR spectrum (CH_2Cl_2) the iridium hydride stretch was observed as a weak band at 2040 cm^{-1}.

When the reaction of **12** (7.9 × 10^{-3} M) and methylamine (0.19 M) in chloroform-d_1 was monitored at −5 °C by ^1H NMR spectroscopy, **12** was rapidly converted to a new species, which we identify as Ir(CR=CRCR=CR)$(PPh_3)_2$[C=CH$(CH_2)_2$O]-[=C$(CH_2)_3$O] (**23**) on the basis of vinyl ether ligand resonances at δ 3.69 (br s, 1 H, IrC=C*H*), 3.26 (br t, J = 9 Hz, 2 H, OCH_2CH_2CH=), and 2.22 (br t, J = 9 Hz, 2 H, OCH_2CH_2CH=) and carbene ligand resonances at δ 4.14 (t, J = 8.0 Hz, 2 H), 2.91 (t, J = 8 Hz, 2 H), and 1.28 (p, J = 8 Hz, 2 H). These assignments are consistent with the vinyl ether ligand resonances observed for **15** and the carbene ligand resonances for **7**. Intermediate **23** was then cleanly converted to **19** and **20** in a first-order process (k = 2.4 × 10^{-4} s^{-1}) at −5 °C, with no detection of additional intermediates. When a similar reaction of **12** (3.5 × 10^{-2} M) and methylamine (0.29 M) in chloroform-d_1 at −5 °C was monitored by ^1H NMR spectroscopy, conversion of **23** to **19** and **20** occurred with an observed first-order rate constant of 2.5 × 10^{-4} s^{-1}.

Scheme V. Reaction of the Mixed Bis(carbene) Complex **13** with Methylamine



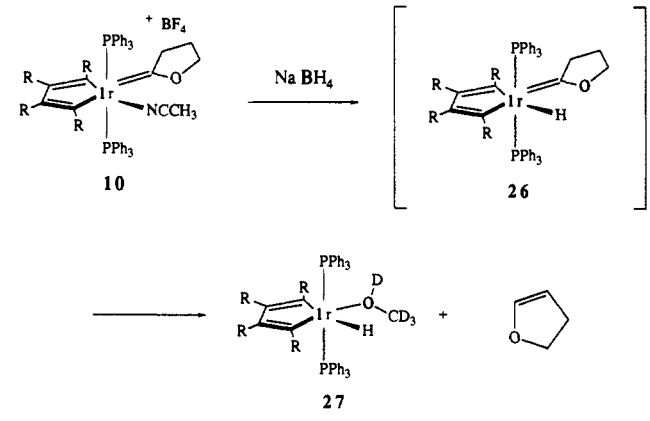
13 **24** (E or Z) **25** (E or Z)

An isotope labeling experiment was employed to determine the source of the hydride ligand in **22**. The isotopically labeled complex $Ir(CR{=}CRCR{=}CR)(PPh_3)_2[{=}CCD_2(CH_2)_2O]_2^+BF_4^-$ (**12**-d_4) was readily prepared from **12** by stirring a two-phase mixture of water-d_2 and chloroform that contained **12** at 23 °C for 17 h. When a preequilibrated mixture of water-d_2 (0.17 mL) and 40% CH_3NH_2 (aqueous, 15 μL) was added to a $CDCl_3$ solution of **12**-d_4 (7.4×10^{-3} mmol, 16 mM) at 23 °C and the solution examined by ^1H NMR spectroscopy, resonances consistent with clean formation of **19**-d_2 and **20**-d_3 were observed. Singlets at 2.87, 3.17, 3.38, and 3.57 ppm were assigned to the methylcarboxylate hydrogens and a resonance at δ −10.6 (t, J = 11 Hz, 1 H) was assigned to the hydride ligand. The resonance at 1.71 ppm (Ir-N$H_2$$CH_3$) for **19** was not observed, and with the exception of resonances at 6.43 (CH=CHCH$_2$) and 2.62 ppm ($OCH_2CH_2CH_2C$=), all of the resonances attributed to **20** were present in the proper intensity ratios. Thus, deuterium was incorporated only into the sites indicated for **19**-d_2 and **20**-d_3 in Scheme IV.

In an effort to recycle the iridium-containing products we examined the reactivity of **19** toward acids. When HCl gas was bubbled through a chloroform solution of **19** for 30 s, the solution color immediately changed from yellow to deep red, with concomitant formation of a precipitate. The volatiles were removed under vacuum and the residue was extracted with ~20 mL of chloroform. The chloroform slurry was filtered and the solvent removed on a rotary evaporator to give a red powder which, when washed with hexanes, gave **1** (92%) as a red-orange solid. In a similar fashion, when acetonitrile slurries of **19** were treated with HBF_4, the mixture was rapidly converted to a clear solution, which yielded bis(acetonitrile) complex **6** upon workup (71%). No attempt was made to maximize the isolated yield of **6**; however a similar ^1H NMR reaction of **19** and HBF_4 indicated quantitative conversion to **6**. Thus, the hydride product **19** is conveniently converted back into either the original metallacycle–halide starting compound **1** by treatment with HCl gas or the bis(acetonitrile) cation **6** by treatment with HBF_4.

7. Reactivity of Bis(carbene) Complex 13 toward Amines. The mixed bis(carbene) complex **13** underwent reaction with methylamine in a manner similar to bis(carbene) **12**; however, in the case of **13** two isomeric coupling products, **24** and **25**, were generated (Scheme V). Thus, when methylamine (40% aqueous solution, 0.033 mmol) was added to a chloroform-d_1 solution of **13** (3.2×10^{-3} mmol, 5.9 mM), after 0.5 h quantitative conversion to iridium hydride **19** and coupling products **24** (45%) and **25** (55%) was observed by ^1H NMR spectroscopy on the crude reaction mixture. In a preparative-scale reaction, methylamine gas (3.5 mmol) was condensed into a chloroform solution of **13** (0.258 mmol, 0.045 M) at −78 °C and after 10 min the solution was allowed to warm to room temperature. The solvent was then removed under vacuum at 0 °C, and the brown residue was heated at ~60 °C (0.004 mmHg) to distill the organic products, which were collected as a colorless liquid (54% combined yield of **24** and **25**). The remaining brown residue was extracted with chloroform and filtered, and hexanes were added to precipitate the iridium hydride product **19** in 64% yield. The ^1H and ^{13}C NMR spectroscopic assignments were made on the mixture of isomers (44:56 ratio of **24** to **25**) by analogy to the resonances observed for **20**. In the ^1H NMR spectrum of the mixture, vinyl hydrogen resonances at δ 5.84 (m, 1 H) and 6.39 (dt, J = 6, 2.3 Hz, 1 H) are assigned to **24** and resonances at δ 5.77 (br d, J = 5 Hz, 1 H) and 6.35 (dd, J = 6.3, 2 Hz, 1 H) are assigned to the vinyl hydrogens of **25**. The methyl hydrogens appear as two doublets with the downfield signal at δ 1.27 (J = 6.6 Hz) assigned to the allylic methyl hydrogens of **25** and the δ 1.26 (J = 6.0 Hz) resonance assigned to **24**. As was the case for carbene coupling product **20**, the spectroscopic data on **24** and **25** do not allow unambiguous determination of alkene stereochemistry. In the ^{13}C NMR spectrum of the mixture two, nine-resonance sets of signals were observed with the ring carbon assignments again made by analogy to the ^{13}C NMR spectrum of **20**. In addition to NMR spectroscopy, the two isomers were characterized by GC–MS analysis of the mixture. The two compounds were readily separated on a Carbowax column, with the major isomer (60.6%) moving more rapidly (retention time 10.9 min) than the minor isomer (39,4%, retention time 11.2 min). The GC traces were correlated with **25** and **24**, respectively, on the basis of the fragmentation patterns in the mass spectra. Both isomers exhibited parent ions at m/z 152; however, the major isomer (**25**) also exhibited an intense fragment peak at m/z 137 ($M^+ - CH_3$), indicative of an allylic substituent, whereas in the spectrum of the minor isomer (**24**) this fragment ion was absent.

Scheme VI. Reaction of Carbene **10** with Sodium Borohydride



10 **26** **27**

8. Reaction of 10 with $NaBH_4$. The carbene–acetonitrile complex **10** reacts with sodium borohydride to give a 90% yield of 2,3-dihydrofuran. Addition of sodium borohydride (0.185 mmol) to a methanol-d_4 solution of **10** (0.032 mmol, 68 mM) resulted in slow formation of a transient iridium hydride species at 23 °C, as indicated by a resonance at δ −11.04 (t, J = 16 Hz) in a ^1H NMR spectrum of the sample. In addition, resonances were observed in the ^1H NMR spectrum at δ 3.99 (t, J = 8 Hz, 2 H), 1.56 (m), and 0.28 (m, 2 H), which we attribute to the formation of a carbene ligand. On the basis of the NMR data we assign a carbene–hydride structure, $IR(CR{=}CRCR{=}CR)(PPh_3)_2(H)[{=}C(CH_2)_3O]$ (**26**), to this complex (Scheme VI). The relative intensities of the hydride resonance at −11.04 ppm and the 1.56 ppm carbene α-methylene resonance to the 3.99 ppm (2 H) methylene hydrogen resonance indicated ~20% deuterium incorporation at the hydride site and 57% deuterium incorporation at the α-methylene site. In addition to the signals assigned to **26**, resonances due to 2,3-dihydrofuran, starting complex **10**, and an additional hydride complex (**27**, present in a trace quantity) were observed in the initial ^1H NMR spectrum. Intermediate **26** slowly decomposed at 23 °C (48 h) to give a 92% yield (NMR) of **27** and a 90% yield of 2,3-dihydrofuran. The presence of 2,3-dihydrofuran was confirmed by addition of an authentic sample to

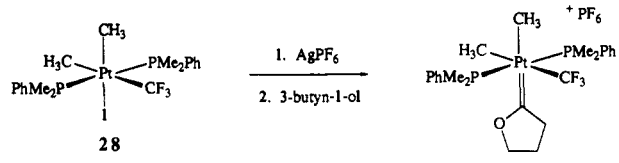
the NMR tube and observation of an intensity increase for the appropriate resonances in the NMR spectrum of the sample. The structure assignment for **27** is consistent with its conversion to hydride **19** in the presence of methylamine. Evaporation of the volatiles from the NMR tube that contained the crude reaction mixture was followed by addition of chloroform solvent and methylamine (40% aqueous solution, 0.75 mL). After 10 min at 23 °C the aqueous phase was removed and the volatiles were evaporated. Addition of chloroform-d_1, followed by ^{1}H NMR spectroscopy on the sample, indicated iridium hydride **19** as the major iridium-containing product. When sodium borodeuteride was employed in a similar NMR tube reaction the resonances attributed to intermediate **26** were observed with the exception of the −11.04 ppm hydride resonance.

When THF-d_8 was employed as the solvent in a similar reaction between sodium borohydride (0.077 mmol) and **10** (0.011 mmol, 77 mM) at 0 °C, ^{1}H NMR spectroscopy on the sample indicated nearly quantitative conversion of **10** to hydride **26** within 15 min. In the ^{1}H NMR spectrum the hydride resonance was observed at δ −10.90 (t, J = 16 Hz, 1 H) and the carbene resonances were observed at δ 3.95 (t, J = 8 Hz, 2 H), 1.61 (t, J = 8 Hz, 2 H), and 0.42 (p, J = 8 Hz, 2 H). In this nonprotic NMR solvent there was no evidence for incorporation of deuterium into either the hydride or the carbene hydrogen sites, as was observed in methanol-d_4. Upon warming the sample to room temperature a rapid decomposition of **26** occurred to give a number of unidentified products, presumably the result of subsequent reaction of the initial products with the excess $NaBH_4$.

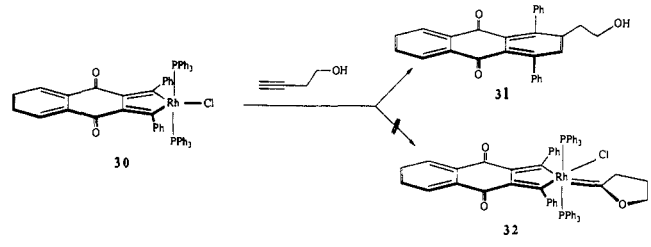
Discussion

1. Synthesis and Structure of Metallacycle–Carbene Complexes. Metallacycles are attractive precursors to metallacycle–carbene complexes due to the large number of metallacyclopentadiene complexes accessible via literature preparations.[17] Collman's iridiacyclopentadiene complex **1**[11] appeared to be a promising carbene complex precursor on the basis of the following: (a) it is coordinatively unsaturated and therefore does not require ligand loss prior to introduction of a carbene ligand, (b) iridium is a third row element and therefore expected to give relatively stable metallacycle–carbene complexes, and (c) the presence of a halide ligand in **1** affords a convenient route into cationic metallacycle–carbene complexes and provides ready access to two cis-coordination sites for the preparation of bis(carbene) complexes. Cationic metallacyclopentadiene complexes were unknown at the time that we first reported the synthesis of **3** and **4** from **2**; this despite their obvious potential for the preparation of metallacycle complexes that contain an additional carbon-bound hydrocarbon ligand.[8a] Chloride ion abstraction from **1** and **2** with $AgBF_4$ proceeds readily and in high yield to provide access to the cationic metallacyclopentadiene complexes **3–6**. The ^{13}C NMR chemical shifts of the metallacycle α-carbons are diagnostic of the π-electron distribution in the ring. For example, Singleton reported the ruthenium metallacyclopenta*triene* complex $(\eta^5\text{-}C_5H_5)Ru(CPhCHCHCPh)(Br)$, which exhibits a resonance in the ^{13}C NMR spectrum at 271 ppm, indicative of carbenoid character at the α-carbons.[18,19] Dissociation of the labile ligand in **3–5** could potentially lead to a metallacyclopentatriene structure with an 18-electron metal count; however, the relatively high field ^{13}C NMR chemical shifts observed for the α-ring carbons (130–165 ppm) allows exclusion of a cyclotriene formulation for **1** as well as **3–5** in the solvents employed herein. This observation is in agreement with EHMO calculations reported by Curtis for d^6 metallacycles.[20]

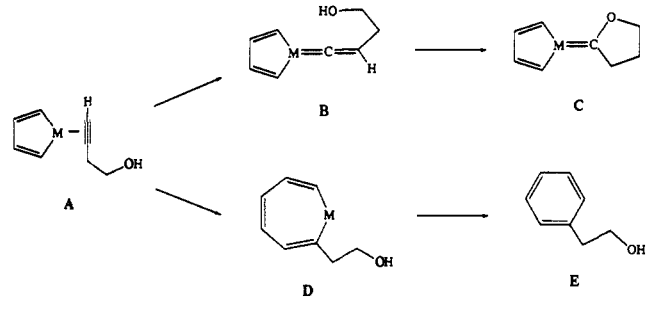
Potential side reactions at the methoxycarbonyl ring substituents in metallacyclopentadiene complexes **1**, **4**, and **5** led us to consider relatively nonnucleophilic reagents for introduction of a carbene ligand. Alkynols are ideally suited for this purpose, as first demonstrated by Clark and Chisholm for conversion of $Pt(CH_3)_2(CF_3)(I)[P(CH_3)_2C_6H_5]_2$ (**28**) to $Pt(CH_3)_2(CF_3)[=C(CH_2)_3O][P(CH_3)_2C_6H_5]_2^+PF_6^-$ (**29**).[21]



Unlike complex **28**, the reaction of a metallacyclopentadiene complex with an alkynol carbene precursor may lead to competitive alkyne insertion into the metallacycle ring followed by reductive elimination to an aromatic six-membered ring.[22] Indeed, this reaction pathway is observed for the reaction of rhodium metallacyclopentadiene complex **30**[23] and 3-butyn-1-ol, which results in formation of the substituted anthraquinone system **31**.[24] There was no spectroscopic evidence for formation of the desired 2-oxacyclopentylidene ligand (**32**).



In contrast to **30**, the iridiacyclopentadiene analogues with four methoxycarbonyl ring substituents, (**1**, **4**, **5**) give excellent yields of metallacycle–carbene complexes (**8–11**) upon reaction with either 3-butyn-1-ol or 4-pentyn-2-ol. As discussed by others,[21] the conversion of alkynols to 2-oxacyclopentylidene ligands can be rationalized by coordination of the alkyne to the transition metal, formation of a vinylidene intermediate, and intramolecular attack by the hydroxyl group at the electrophilic vinylidene carbon to form the carbene ligand (A to B to C). In the case of **30**,



(17) (a) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (c) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157, and references therein. (d) Schore, N. E. *Chem. Rev.* **1988**, 88, 1081, and references therein. (e) Negishi, E.; Takahashi, T. *Synthesis* **1988**, *1*, 1. (f) Sikora, D. J.; Raush, M. D. *J. Organomet. Chem.* **1984**, *276*. (g) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (h) Chappell, S. D.; Cole-Hamilton, D. *Polyhedron* **1982**, *1*, 739, and references therein.

(18) Thorn and Hoffmann have calculated the electronic structure of d^6 metallacyclopentadiene complexes: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

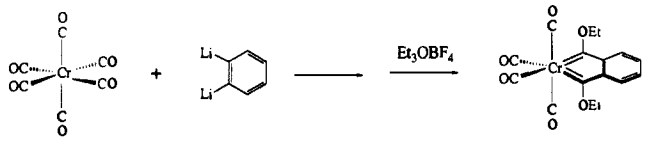
(19) (a) Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (b) For additional examples of metallacyclopentatriene complexes, see: Reference 16. Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

(20) (a) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (b) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668.

(21) (a) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532. (b) Clark, H. C.; Reimer, K. J. *Inorg. Chem.* **1975**, *14*, 2133. (c) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *47*, C17. (d) Marten, D. F. *J. Chem. Soc., Chem. Commun.* **1980**, 341. (e) Oguro, K.; Wada, M.; Okawara, R. *J. Organomet. Chem.* **1978**, *159*, 417. (f) Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605. (g) Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424.

insertion of the alkyne into the metallacycle ring (A to D to E) may be rapid relative to the rate of a 1,2 hydrogen shift. However, thermodynamic control of product formation cannot be ruled out, particularly in light of a recent report by Bullock that describes a reversible alkyne to vinylidene transformation in a ruthenium system.[25]

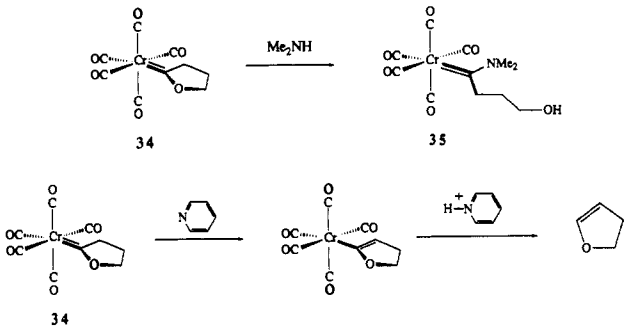
2. Synthesis and Structure of Metallacycle–Bis(carbene) Complexes. Bis(carbene) complexes remain highly illusive species primarily because the classic Fischer route toward this compound class relies on nucleophilic attack at a coordinated carbon monoxide ligand followed by quenching with an electrophile. The highly electrophilic nature of alkoxycarbenes results in preferential attack of a nucleophile at the carbene carbon rather than at a carbon monoxide ligand in monocarbene substrates.[26] These limitations have been somewhat overcome by employment of dianion reagents in reactions with metal carbonyl complexes.[27] For example, Fischer reported the reaction of *o*-dilithiobenzene and hexacarbonylchromium followed by alkylation with triethyloxonium tetrafluoroborate to give bis(alkoxycarbene) complex **33**.[27a]



33

Employment of alkynol cyclization methodology circumvents the inherent limitations in the classic Fischer carbene synthesis and is therefore an excellent route toward bis(alkoxycarbene) complexes. The bis(acetonitrile) complex **5** appeared well suited as a precursor to a bis(2-oxacyclopentylidene) complex in light of the successful use of carbonyl–acetonitrile complex **4** as a carbene precursor. Although the axial triphenylphosphine ligands afford a degree of steric bulk above and below the equatorial plane that contains the labile acetonitrile ligands, the metallacycle ring constrains the carbon–iridium–carbon angle to ~77° and therefore provides a degree of access at the metal center for alkyne coordination and rearrangement. Indeed, chloroform solutions of **5** undergo reaction with excess 3-butyn-1-ol at 50 °C to give the bis(carbene) complex **12** in 87% isolated yield. Mixed bis(alkoxycarbene) complexes present a greater degree of synthetic challenge than bis(carbene) complexes that contain identical carbene ligands. To our knowledge, no examples of mixed bis(alkoxycarbene) complexes have been reported in the literature prior to the synthesis of **13** reported here.

3. Reactivity of Metallacycle–Carbene Complexes toward Nucleophiles. The reactions of alkoxycarbene complexes with amines typically result in deprotonation at the α-carbon, nucleophilic attack at the carbene carbon, or nucleophilic attack at the sp^3 carbon–oxygen bond. For example, Dötz recently reported the reaction of 2-oxacyclopentylidene complex **34** with dimethylamine to give the ring-opened (dimethylamino)(hydroxypropyl)carbene complex **35**.[21g] This result contrasts with Fischer's earlier finding that **34** reacts with pyridine to give dihydrofuran,[28] presumably via initial deprotonation of the carbene ligand followed by protonation of the metal–carbon bond.[29]



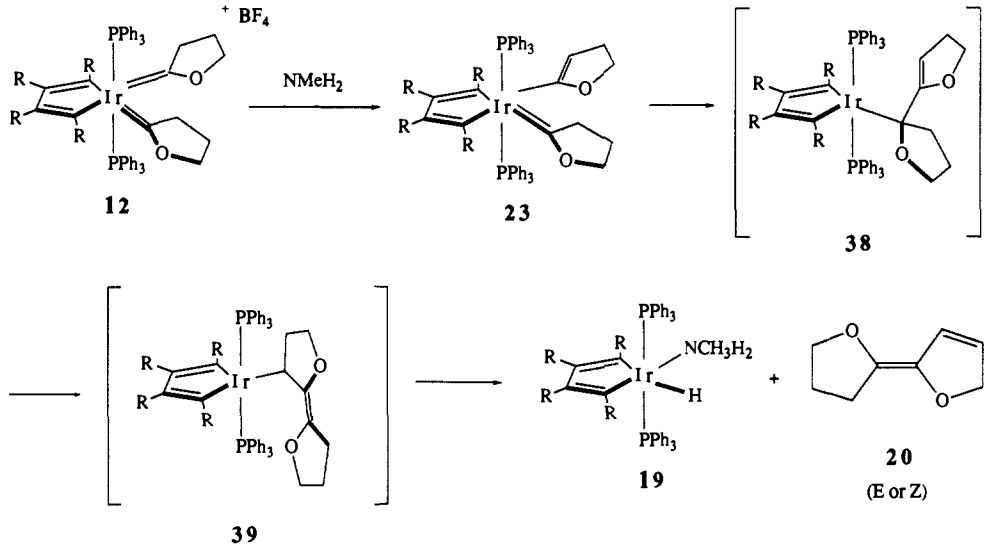
34 **35**

34

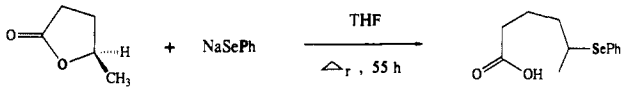
In contrast to the reactions of the neutral 2-oxacyclopentylidene complex **34** with amines, the cationic 2-oxacyclopentylidene complex **8** undergoes reaction with pyridine to give the ring-opened pyridinium-substituted acyl complex **14**. This transformation is presumably the result of S_N2 attack by pyridine at the carbon–oxygen bond of the oxacyclopentylidene ligand. This mode of alkoxycarbene reactivity is common for methoxycarbenes[30-32] and has previously been observed for reactions of the 2-oxacyclopentylidene ligand with non-amine nucleophiles.[32] In reaction with amines deprotonation at the acidic α-carbon of the carbene ligand is expected to compete with nucleophilic attack at the carbon–oxygen bond. For **8**, deprotonation by pyridine to give the neutral vinyl ether complex **15** is the kinetically preferred reaction. However, this deprotonation reaction is reversible under the reaction conditions and at longer times the equilibrium mixture of carbene and vinyl ether complex is drained off to the pyridinium–acyl species, **14**. The fate of the oxacyclopentylidene ligand therefore depends on the acidity of both the carbene ligand and the conjugate acid of the amine. When $P(CH_3)_3$ or imidazole are employed as the base, no acyl product is observed and high yields of the neutral vinyl ether complexes are isolated. The reaction outcome is also controlled by simple choice of solvent. When benzene is employed as solvent, the pyridinium cation generated in the initial deprotonation step is insoluble and precipitates from solution, thereby shifting the equilibrium to the vinyl ether complex. The mild conditions of the carbene to acyl conversion led us to explore the effect of additional substitution at the carbon center that undergoes nucleophilic attack. The methyl-substituted carbene **9** reacts with pyridine at 23 °C to generate an equilibrium mixture of **9** and vinyl ether complex **18**. At refluxing chloroform temperature the equilibrium mixture is once again drained off to a pyridinium-substituted acyl product. The mild reaction conditions required for this transformation are remarkable based on the established reactivity trends for organic lactones and are an indication of the highly electrophilic character

(22) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539, and references therein.
(23) Müller, E. *Synthesis* **1974**, 761.
(24) O'Connor, J. M.; Johnson, J. A., unpublished results.
(25) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.
(26) For exceptions, see: (a) Fischer, E. O.; Kreissl, F. R.; Kreiter, C. G.; Meineke, E. W. *Chem. Ber.* **1972**, *105*, 2558. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2160. (c) Darst, K. P.; Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *J. Organomet. Chem.* **1980**, *195*, 317. (d) Lappert, M. F.; Pye, P. L.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1272.
(27) (a) Fischer, E. O.; Röll, W.; Schubert, U.; Ackermann, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 611. (b) Fischer, E. O.; Röll, W.; Hoa Tran Huy, N.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 2951. (c) Schubert, U.; Ackermann, K.; Hoa Tran Huy, N.; Röll, W. *J. Organomet. Chem.* **1982**, *232*, 155. (d) Hoa Tran Huy, N.; Pascard, C.; Tran Huu Dau, E.; Dötz, K. H. *Organometallics* **1988**, *7*, 590.
(28) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.
(29) (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (b) Casey, C. P. In *New Applications of Organometallic Reagents in Organic Synthesis*; Journal of Organometallic Chemistry Library; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; Vol. 1.
(30) For representative examples, see: Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188. Green, M. L. H.; Mitchard, L.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794. Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199. Chisholm, M. H.; Clark, H. C.; Johns, W. S.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 900. Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.
(31) (a) Fischer, E. O.; Selmayr, T.; Kreissel, F. R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574. (b) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857.
(32) (a) Moss, J. R. *J. Organomet. Chem.* **1982**, *231*, 229. (b) Bailey, N. A.; Chell, P. L.; Manuel, C. P.; Mukhopadhyay, A.; Rogers, D.; Tabbron, H. E.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2397. (c) Game, C. H.; Green, M.; Moss, J. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 351. (d) Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1975**, *97*, 421.

Scheme VII. Proposed Mechanism for Conversion of **12** to **19** and **20**



of the cationic iridium center. Related S_N2-type ester cleavage reactions that employ halide and amine nucleophiles work well only with methyl esters or, to a lesser extent, ethyl esters.[33] Powerful nucleophiles such as phenyl selenide or Lewis acids in combination with thiols will induce S_N2 ester cleavage reactions even at secondary carbon centers.[34] For example, the reaction of phenyl selenide and methyl-substituted butyrolactone **36** requires 55 h in refluxing THF for conversion to the phenylselenenyl carboxylic acid **37**.[34a]



36 37

4. Reactivity of Metallacycle–Carbene Complexes toward Amines. The reaction of bis(carbene) **12** toward pyridine is among the most fascinating, discovered to date, for the 2-oxacyclopentylidene ligand and one that points the way to development of a new class of carbene coupling reactions. The reaction of **12** and pyridine results in formation of the iridium hydride complex **22** (46%) and the carbene coupling product 2-(2(5*H*)-furanylidene)tetrahydrofuran (**20**; 46%). When methylamine is employed as the base in place of pyridine the reaction is rapid even at −5 °C and results in quantitative conversion to **20** and iridium hydride **19**. On the basis of a low-temperature ^{1}H NMR spectroscopic study, we propose an initial, rapid deprotonation of one of the carbene ligands to generate the neutral vinyl ether–carbene complex **23** (Scheme VII). Intermediate **23** is then rapidly converted to **20** and **19** in a first-order process for which no additional intermediates are observed by NMR spectroscopy.

The deprotonation step is consistent with the observation that mono(carbene) complexes **8** and **9** also undergo a rapid deprotonation by pyridine to generate neutral vinyl ether complexes **15** and **18**. However, whereas **15** and **18** are eventually converted to the acyl complexes **14** and **17**, the neutral vinyl ether–carbene complex **23** has an alternative reaction path available: migration of the vinyl ether ligand to the carbene carbon to give a new intermediate **38**.[35] Complex **38** has β-hydrogens available for abstraction by iridium; however, on the basis of a deuterium labeling study, the β-hydrogen abstraction must be reversible or slow relative to a 1,3 iridium shift, possibly via a π-allyl intermediate, to give **39**. Part of the driving force for this migration would arise from relief of steric congestion on going from a trisubstituted carbon to a secondary carbon bound to iridium. It is at this stage that the stereochemistry of the alkene is fixed. We do not know with certainty the stereochemistry in **20**; however, on the basis of negative NOE evidence, we favor the *E* isomer as shown in Scheme VII. Intermediate **39** then undergoes a β-hydrogen abstraction to directly give the observed products, **19** and **20**. Compound **20** is, not surprisingly, oxidized in the air to the furan **21**.

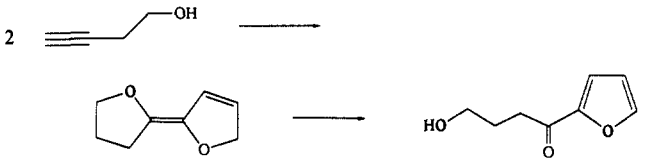
The intramolecular nature of this unusual coupling reaction was confirmed by a crossover experiment in which the mixed bis(carbene) complex **13** was employed as the substrate. Once again a rapid reaction is observed with methylamine to give **19** quantitatively, as well as the two expected carbene coupling products, **24** and **25**, in a 44:56 ratio, as determined by ^{1}H NMR spectroscopy. There was no evidence for crossover products by GC–MS analysis of the product mixture. The iridium hydride product **19** is conveniently converted back to the immediate bis(carbene) precursor **5** by treatment with HBF_4 in acetonitrile solution. Alternatively, by simply bubbling HCl gas through chloroform solutions of **19**, Collman's metallacycle, **1**, is reformed quantitatively. The net transformation of the organic substrate is conversion of 2 equiv of alkynol to the bicyclic heterocycle **20** and substituted furan **21**.

The main difference between mono(carbene) complexes **8** and **9** and bis(carbene) complexes **12** and **13**, in reactions with amines, arises subsequent to deprotonation of the carbene ligand. The mono(carbene) complex intermediates (**15** and **18**) do not undergo

(33) (a) McMurry, J. *Org. React.* **1977**, *24*, 187. Friedrich, E. C.; Delucca, G. *J. Org. Chem.* **1983**, *48*, 1678. (b) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979** *44*, 1247.

(34) (a) Liotta, D.; Sunay, U.; Santiesteban, H.; Markiewicz, W. *J. Org. Chem.* **1981**, *46*, 2605. (b) Node, M.; Nishide, K.; Ochiai, M.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1981**, *46*, 5163.

(35) For alkyl migrations to carbene carbons, see: (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43. (c) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (d) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (e) Thorn, D. L. *Organometallics* **1986**, *5*, 1897. (f) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (g) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (h) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. (i) Werner, H.; Kletzin, H.; Höhn, A.; Paul, W.; Knaup, W.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1986**, *306*, 227. (j) Werner, H.; Roder, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686. (k) Davey, C. E.; Osborn, V. A.; Winter, M. J.; Woodward, S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, Netherlands, 1989; p 159. (l) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723. (m) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 7730. (n) Maitlis, P. M.; Bailey, N. A.; Adams, H.; Martinez, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 286. (o) Davey, C. E.; Osborn, V. A.; Winter, M. J.; Woodward, S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, Holland, 1989, p 159.

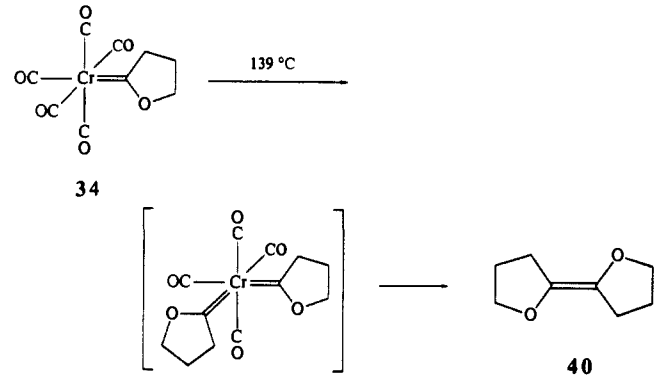


20 21

vinyl ether ligand migration to the cis carbonyl ligand, whereas the bis(carbene) complex intermediates (e.g., **23**), do undergo vinyl ether ligand migration to the cis carbene ligand. This difference in migratory behavior is consistent with Werner's recent observation that $[(\eta^6\text{-}C_6H_6)Os(CO)(=CH_2)(CH_3)]^+PF_6^-$ undergoes alkyl migration to the carbene ligand in preference to the carbonyl ligand.[35j]

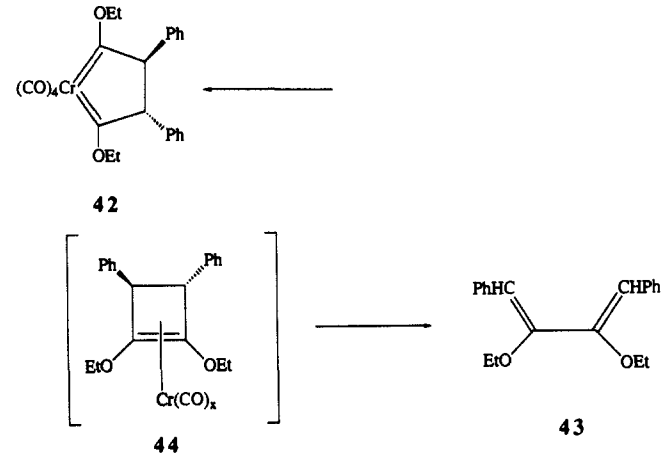
The reaction of sodium borohydride with mono(carbene) **10** results in formation of an iridium hydride product **27** and dihydrofuran. A low-temperature ^1H NMR study provided support for the formation of a carbene–hydride intermediate **26**, which is converted to the observed products without observation of additional intermediates. The mechanism of this transformation is presumably similar to the conversion of **23** to **19** and **20**: migration of the hydride ligand to the carbene carbon followed by β-hydrogen abstraction.[36]

Carbene ligand coupling reactions are well documented for the thermolysis of mono(carbene) complexes.[37] For example, the thermolysis of chromium carbene **34** at 139 °C led to a 50% yield of the carbene ligand coupling product **40**, as a mixture of *E* and *Z* isomers. Kinetic and isotope labeling studies led Casey to propose a bis(carbene) intermediate **41** for the **34** to **40** conversion.[29]



34 41 40 (E and Z)

To our knowledge, there is only one report of carbene ligand coupling in an isolable mononuclear bis(carbene) complex. Hoa Tran Huy found that heating the chelating bis(carbene) complex **42** led to isolation of the diene product **43** and its mono- and bis chromium tricarbonyl complexed analogues.[38] The observed products were proposed to arise from an alkene intermediate, **44**, which undergoes conrotatory ring opening.



42 44 43

Conclusion

In conclusion, the first isolable metallacycle–carbene complexes have been synthesized and fully characterized, both in solution and in the solid state.[39] The use of alkynols as carbene ligand precursors provides access to metallacycle–bis(carbene) complexes, including the first example of a mixed bis(alkoxycarbene) complex. These electrophilic bis(carbene) complexes undergo an unprecedented, base-induced, carbene–carbene ligand coupling process. Results from labeling, crossover, and low-temperature NMR experiments indicate the most probable mechanistic pathway to be an intramolecular reaction involving carbene ligand deprotonation, alkyl to carbene ligand migration, a 1,3 iridium shift, and β-hydrogen elimination. These results point the way to the development of a new class of carbene coupling reactions, which will complement and extend the currently established array of carbene ligand transformations.

Experimental Section

General Data. All reactions and reaction workups were performed in the air unless otherwise noted. Organic solvents were obtained commercially and used without further purification unless otherwise indicated. IR spectra were recorded on a Perkin-Elmer 1330 spectrometer. NMR spectra were recorded on a GE QE 300 (^1H, 300 MHz; ^{13}C, 75.5 MHz; ^{31}P, 122 MHz) spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to residual protio-solvent signal, and ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 (internal capillary). GC–MS data were obtained on a HP Hiltecal 5988 instrument using a Carbowax 20M column. FAB mass spectra were performed at the University of California, Riverside Mass Spectroscopy Facility. Elemental analyses were performed by Schwarzkopf, Dessert Analytics, or Galbraith Laboratories, Inc.

Deuterated water, 3-butyn-1-ol, 4-pentyn-2-ol, and methylamine were obtained from Aldrich Chemical Co; silver tetrafluoroborate was obtained from Strem Chemicals, 4-pentyn-1-ol from Lancaster Synthesis, and ^{13}CO (99% ^{13}C) from Isotec Inc. Pyridinium tetrafluoroborate was prepared by reaction of HBF_4 and pyridine.

Preparation of $Ir(CR{=}CRCR{=}CR)(PPh_3)_2(CO)(OH_2)^+BF_4^-$ (3, R = CO_2CH_3). To a yellow methylene chloride solution (25 mL) of **2** (440 mg, 0.41 mmol, 17 mM) was added silver tetrafluoroborate (90 mg, 0.46 mmol). The mixture was stirred for 2 h at 23 °C, during which time a grey precipitate formed. Filtration of the slurry through Celite, evaporation of the orange filtrate, and recrystallization of the residue from THF/hexanes gave **3** contaminated by silver salts. The impure product was dissolved in methylene chloride and the solution exposed to the air for ~24 h, during which time an additional grey precipitate of silver salts formed. Filtration of the solution through Celite and recrystallization from THF/hexanes gave **3** (328 mg, 0.29 mmol, 70%) as a yellow solid: mp (sealed capillary) 172–174 °C (dec); ^1H NMR ($CDCl_3$) δ 7.4–7.5 (m), 6.41 (br, OH_2), 3.74 (s, 3 H), 3.41 (s, 3 H), 3.17 (s, 3 H), 3.07 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 172.9 (t, J = 8.2 Hz, Ir–*C*O), 172.6, 168.9, 168.3, 164.5, 157.7, 149.3 (br), 146.3 (br), 143.5 (t, J = 10.9 Hz, Ir—*C*(R)=), 134.3 (t, $J_{PC+P'C}$ = 9.9 Hz), 131.5, 128.7 (t, $J_{PC+P'C}$ = 9.9 Hz), 126.8 (t, $J_{PC+P'C}$ = 57.9 Hz), 52.7, 51.89, 51.80, 51.43; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −7.8 (s); IR (CH_2Cl_2) 2070 (s), 1706 (s) cm^{-1}; MS-(FAB), *m/e* calcd for $C_{49}H_{44}O_{10}P_2IrBF_4 - BF_4 - H_2O$ 1029.1933, obsd 1029.1854. Anal. Calcd for $C_{49}H_{44}O_{10}P_2IrBF_4$: C, 51.92; H, 3.88; P, 5.47. Found: C, 51.59; H, 3.88; P, 5.47.

Preparation of $Ir(CR{=}CRCR{=}CR)(PPh_3)_2(CO)(NCCH_3)^+BF_4^-$ (4, R = CO_2CH_3). To a yellow acetonitrile slurry (70 mL) of **2** (1.05 g, 0.99

(36) For hydride migrations to carbenes, see: (a) Copper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761; *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335. (c) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (d) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1011. (e) Le Bozec, H.; Filllaut, J.-L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1182. (f) Osborn, V. A.; Parker, C. A.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1185. (g) References 13 and 30c,k.

(37) (a) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Perkin Trans. 1* **1973**, 17. (b) Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem.* **1972**, *36*, C4. (c) Reference 24.

(38) Hoa Tran Huy, N.; Lefloch, P.; Louis, J. M.; Fetizon, M. *J. Organomet. Chem.* **1986**, *311*, 79.

(39) Metallacycle–carbenes have been proposed as intermediates in the thermal decomposition of nickelacyclohexanes: Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

mmol, 14 mM) was added silver tetrafluoroborate (260 mg, 1.34 mmol). The mixture was stirred at 23 °C for 12 h, during which time a grey precipitate formed. Filtration of the slurry through Celite in the air and evaporation of the volatiles gave product contaminated by silver salts. An acetonitrile solution of the impure product was exposed to the air for 24 h, whereupon an additional precipitation of silver salts occurred. A second filtration through Celite, concentration of the filtrate by rotary evaporation, and addition of hexanes led to isolation of **4** (1.1 g, 0.95 mmol, 96%) as an off-white solid: mp (sealed capillary) 189–193 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.4–7.5 (m), 3.50 (s, 3 H), 3.49 (s, 3 H), 3.24 (s, 3 H), 3.19 (s, 3 H), 2.04 (s, 3 H, $NCCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.2, 169.0 (s), 169.0 (t, J = 8.3 Hz), 166.8, 164.2, 162.6 (t, J = 9.0 Hz), 154.7 (br), 150.1 (t, J = 2.0 Hz), 134.4 (t, $J_{PC+P'C}$ = 10.3 Hz), 132.7 (t, J = 8.0 Hz), 131.6, 128.5 (t, $J_{PC+P'C}$ = 10.7 Hz), 126.5 (t, $J_{PC+P'C}$ = 59.1 Hz), 124.2, 52.0, 51.4, 51.3, 51.2, 3.54; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −7.9 (s); IR (CH_2Cl_2) 2082 (s), 1712 (s) cm^{-1}; MS(FAB), *m/e* calcd for $C_{51}H_{45}NO_9P_2IrBF_4 - BF_4 - NCCH_3$ 1029.1933, obsd 1029.1976. Anal. Calcd for $C_{51}H_{45}NO_9P_2IrBF_4$: C, 52.94; H, 3.92; N, 1.21. Found: C, 52.73; H, 3.92; N, 1.21.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(NCCH$_3$)$_2^+$BF$_4^-$ (5, R = CO_2CH_3). To a yellow acetonitrile solution (60 mL) of **1** (1.34 g, 1.29 mmol, 22 mM) was added silver tetrafluoroborate (251 mg, 1.29 mmol). The mixture was stirred for 16 h. Filtration of the resultant slurry through Celite led to product contaminated by silver salts. An acetonitrile solution of the impure product was heated (50 °C, 12 h) in the air and then filtered through Celite to remove the black precipitate that had formed. Removal of the solvent on a rotary evaporator and recrystallization of the residue from C_6H_6/hexanes gave **5** (1.12 g, 0.96 mmol, 74%) as a yellow solid: mp 200–203 °C dec; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.4–7.5 (m), 3.39 (s, 6 H), 3.37 (s, 6 H), 1.93 (s, 6 H, $NCCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 172.4, 165.2, 150.3, 142.9 (t, J = 7.5 Hz), 134.8 (br), 130.7, 127.8 (t, $J_{PC+P'C}$ = 8.1 Hz), 126.7 (t, $J_{PC+P'C}$ = 56.7 Hz), 122.7, 50.9, 50.8, 3.5; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −2.78 (s); IR (THF) 1700 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{48}N_2O_8P_2Ir - BF_4$: C, 53.38; H, 4.15; N, 2.40. Found: C, 53.28; H, 4.43; N, 2.13.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)(PMe$_3$)$^+$BF$_4^-$ (6, R = CO_2CH_3). A 100-mL round-bottom flask equipped with a magnetic stir bar was charged with **4** (615 mg, 0.53 mmol, 9 mM) and 60 mL of dry chloroform and cooled to −76 °C. PMe_3 (0.2 mL, 3.5 mmol) was vacuum transferred in and the solution was stirred at 23 °C for 5 h. Removal of the volatiles under vacuum and recrystallization from CH_2Cl_2/hexanes gave **6** as a pink solid (536 mg, 0.45 mmol, 85%): mp (sealed capillary) 192–195 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.4–7.5 (m), 3.47 (s, 6 H), 3.36 (s, 3 H), 3.18 (s, 3 H), 1.24 (d, J = 9.9 Hz, 9 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50 MHz) δ 172.6 (m), 169.6 (d, J = 3.6 Hz), 166.6, 166.3, (d, J = 7.2 Hz), 159.1 (d, J = 8.6 Hz), 155.3, 148.4 (td, J = 10.6, 6.1 Hz), 148.1 (dt, J = 79, 9.2 Hz), 135.2 (t, $J_{PC+P'C}$ = 9.4 Hz), 132.2, 128.9 (t, $J_{PC+P'C}$ = 10.2 Hz), 128.6 (t, $J_{PC+P'C}$ = 57.9 Hz), 52.8, 51.9, 51.3, 19.0 (d, J = 33.8 Hz); ^{31}P NMR ($CDCl_3$) δ −12.8 (d, J = 18 Hz), −72.8 (t, J = 18 Hz); IR (CH_2Cl_2) 2053 (s), 1693 (s) cm^{-1}; MS(FAB), *m/e* (relative intensity) 1105 (M − BF_4, 32), 1029 (M − BF_4 − PMe_3, 100), 1001 (M − BF_4 − PMe_3 − CO, 53), 843 (M − BF_4 − PPh_3, 14), 815 (M − BF_4 − PPh_3 − CO, 30). Anal. Calcd for $C_{52}H_{51}O_9P_3IrBF_4$: C, 52.41; H, 4.28. Found: C, 52.16; H, 4.48.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(Cl)[=C(CH$_2$)$_3$O] (7, R = CO_2CH_3). To a chloroform solution (50 mL) of **1** (778 mg, 0.75 mmol, 15 mM) was added by syringe 3-butyn-1-ol (71 μL, 0.94 mmol). The solution was stirred at 23 °C for 15 h and concentrated by rotary evaporation, and diethyl ether was added to precipitate **7** (731 mg, 0.66 mmol, 88%) as a yellow solid: mp (sealed capillary) 168–170 °C dec; ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.2 (t, J = 6.2 Hz), 175.7, 175.1, 167.7, 163.9, 153.0 (m), 152.4 (t, J = 6.8 Hz), 148.8 (t, J = 12.3 Hz), 135.1, 131.5 (t, $J_{PC+P'C}$ = 55.6 Hz), 129.2, 126.7, 87.2, 55.3, 50.4, 50.1, 49.8, 49.7, 18.2; $^{31}P\{^1H\}$ NMR (acetone-d_6) δ −18.5; IR (CH_2Cl_2) 1703 (vs, br) cm^{-1}. Anal. Calcd for $C_{52}H_{48}O_9P_2ClIr\cdot 0.8CHCl_3$: C, 58.35; H, 4.55. Found: C, 58.55; H, 4.68. The presence of the chloroform solvate in the elemental analysis sample was confirmed by ^{1}H NMR spectroscopy.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[=C(CH$_2$)$_3$O]$^+$BF$_4^-$ (8, R = CO_2CH_3). To a methylene chloride solution (25 mL) of **4** (584 mg, 0.50 mmol, 20 mM) was added by syringe 3-butyn-1-ol (36 μL, 0.48 mmol). The solution was refluxed under nitrogen for ~12 h, the solvent removed by rotary evaporation, and the residue washed with THF to give **8** (573 mg, 0.48 mmol, 96%) as a yellow solid: mp (sealed capillary) 208 °C dec; ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 278.3 (br), 173.8, 171.1, 170.8 (t, J = 6.8 Hz), 167.8, 164.0, 161.5 (t, J = 10.0 Hz), 158.3, 150.8, 140.3 (t, J = 10.0 Hz), 134.2 (br), 131.7 (br), 128.4 (br), 127.3 (t, $J_{PC+P'C}$ = 60.0 Hz), 91.8, 60.9, 51.7, 51.4, 51.1, 19.53; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 11.0; IR (CH_2Cl_2) 2065 (s), 1700 (br s), 1430 (s), 1482 (s) cm^{-1}; MS(FAB), *m/e* calcd for $C_{53}H_{48}O_{10}P_2IrBF_4 - BF_4$ 1099.2352, obsd 1099.2389. Anal. Calcd for $C_{53}H_{48}O_{10}P_2IrBF_4$: C, 53.70; H, 4.05; P, 5.23. Found: C, 53.50; H, 4.09; P, 5.24.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[=C(CH$_2$)$_2$CHCH$_3$O]$^+$BF$_4^-$ (9, R = CO_2CH_3). To a chloroform solution (20 mL) of **4** (186 mg, 0.16 mmol, 8 mM) was added by syringe 4-pentyn-2-ol (83 μL, 0.88 mmol). The solution was refluxed under nitrogen for ~20 h and filtered through a sintered glass frit in the air, and the volatiles were removed by rotary evaporation. The residue was recrystallized from THF/pentane to give **9** (183 mg, 0.15 mmol, 95%) as a yellow solid: mp 155–156 °C dec; ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 278.0 (br), 173.6, 170.5, 170.4, 170.3, 168.1, 164.9, 158.0, 153.4, 143.0, 134.5 (m), 131.7, 128.5 (dd, J = 2.6, 7.6 Hz), 127.7 (m), 103.6, 62.7, 51.6, 51.5, 51.3, 51.2, 28.3, 19.6; IR (CH_2Cl_2) 2065 (vs), 1710 (vs) cm^{-1}; MS(FAB), *m/e* (relative intensity) calcd for $C_{50}H_{50}O_{10}IrP_2BF_4$ 1113 (M − BF_4, 100), 1029 (M − BF_4 − C_5H_8O, 6), 1001 (M − BF_4 − C_5H_8O − CO, 13), 851 (M − BF_4 − PPh_3, 8), 821 (M − BF_4 − CO − $C_{12}H_{12}O_8$, 22).

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(NCCH$_3$)[=C(CH$_2$)$_3$O]$^+$BF$_4^-$ (10, R = CO_2CH_3). To an orange-brown acetonitrile solution (30 mL) of **7** (1.0 g, 0.90 mmol, 30 mM) was added silver tetrafluoroborate (280 mg, 1.4 mmol). The resultant grey slurry was stirred under nitrogen at 23 °C for 15 h. Filtration of the slurry through Celite and evaporation of the volatiles on a rotary evaporator led to a residue contaminated by silver salts. The residue was dissolved in chloroform and the solution was exposed to the air for 24 h, whereupon a black precipitate slowly formed. A second filtration and recrystallization from chloroform/diethyl ether gave **10** (764 mg, 0.64 mmol, 71%) as a yellow solid. An alternative preparation of **10** involved addition of 3-butyn-1-ol (11 mL, 0.17 mmol) by syringe to a chloroform solution (10 mL) of bis(acetonitrile) complex **5** (171 mg, 0.146 mmol, 15 mM). The solution was stirred at 23 °C for ~15 h, the volatiles were removed by rotary evaporation, and the residue was recrystallized from THF/hexanes to give **10** (163 mg, 0.14 mmol, 94%) as a yellow solid: ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 285.2 (t, J = 6.4 Hz), 174.7, 174.0, 167.0, 164.1, 154.0, 148.6 (t, J = 10.6 Hz), 147.8, 147.7 (t, J = 7.5 Hz), 134.5 (t, $J_{PC+P'C}$ = 9.7 Hz), 130.8, 127.9 (t, $J_{PC+P'C}$ = 10.0 Hz), 127.4 (t, $J_{PC+P'C}$ = 57.1 Hz), 122.8, 88.9, 59.0, 50.8, 50.6, 50.5, 19.7, 4.02; IR (CH_2Cl_2) 1700 (s) cm^{-1}; MS(FAB), *m/e* calcd for $C_{54}H_{51}O_9P_2IrBF_4 - BF_4$ 1112.2669, obsd 1112.2721.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(NCCH$_3$)[=C(CH$_2$)$_2$CHCH$_3$O]$^+$BF$_4^-$ (11, R = CO_2CH_3). To a chloroform-d_1 solution (0.33 mL) of bis(acetonitrile) complex **5** (34.3 mg, 0.029 mmol, 89 mM) in an NMR tube was added by syringe 4-pentyn-2-ol (4.9 μL, 0.052 mmol). The solution was maintained at 23 °C for 24 h, at which time ^{1}H NMR spectroscopy on the sample indicated formation of **11** in 91% yield. Removal of the volatiles under vacuum and recrystallization of the residue from the chloroform/hexanes gave **11** as a yellow solid: ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 283.8 (t, J = 6.7 Hz), 173.9, 173.8, 166.8, 164.6, 153.9, 150.4 (t, J = 10.8 Hz), 149.0, 145.8 (m), 134.6 (m), 130.7, 128.0 (m), 127.5 (m), 122.7, 100.1, 60.3, 50.9, 50.8, 50.7, 50.6, 28.3, 19.6, 4.1; MS(FAB), *m/e* calcd for $C_{55}H_{53}O_9NP_2IrBF_4 - BF_4 - NCCH_3$ 1085.2560, obsd 1085.2609.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$[=C(CH$_2$)$_3$O]$_2^+$BF$_4^-$ (12, R = CO_2CH_3). To a chloroform solution (25 mL) of **5** (630 mg, 0.54 mmol, 22 mM) was added by syringe 3-butyn-1-ol (230 μL, 3.0 mmol). The solution was heated at 50 °C for 3.5 h and concentrated by rotary evaporation, and benzene was added to precipitate **12** (575 mg, 0.47 mmol, 87%) as a yellow solid: mp >145 °C dec; ^{1}H NMR and MS, Table I; $^{13}C\{^1H\}$ NMR (CD_3CN) δ 283.8 (t, J = 6.5 Hz), 178.1, 167.0, 153.7 (t, J = 9.9 Hz), 152.1, 135.6 (t, $J_{PC+P'C}$ = 9.6 Hz), 132.0, 129.6 (t, $J_{PC+P'C}$ = 56.8 Hz), 129.0 (t, $J_{PC+P'C}$ = 9.8 Hz), 90.1, 59.3, 51.4, 51.1, 20.9; IR (CH_2Cl_2) 1700 (br) cm^{-1}; MS(FAB), *m/e* calcd for $C_{56}H_{54}O_{10}P_2IrBF_4 - BF_4$ 1141.2777, obsd 1141.2848. Anal. Calcd for $C_{56}H_{54}O_{10}P_2IrBF_4\cdot 3C_6H_6$: C, 60.78; H, 4.96. Found: C, 60.62; H, 4.92. The presence of three C_6H_6 of solvation in the elemental analysis sample is confirmed by integration of the phenyl region of the ^{1}H NMR spectrum.

Preparation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$[=C(CH$_2$)$_3$O][=C(CH$_2$)$_2$CH(CH$_3$)O]$^+$BF$_4^-$ (13, R = CO_2CH_3). To a yellow methylene chloride solution of **7** (76.4 mg, 0.069 mmol, 7.8 mM) was added $AgBF_4$ (947.8 mg, 0.25 mmol). The resultant slurry was stirred at room temperature for 4.5 h and then filtered to remove the AgCl precipitate. The precipitate was washed with an additional 22 mL of methylene chloride, and to the combined methylene chloride solutions was added 4-pentyn-

2-ol (20 μL, 0.25 mmol). After ~16 h at room temperature, the solution was filtered through Celite and concentrated to ~0.5 mL. Addition of diethyl ether led to precipitation of **13** as a yellow solid (69.4 mg, 0.056 mmol, 81%): mp (capillary) >145 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.32 (m), 4.75 (br q, J = 9 Hz, 1 H), 4.63 (q, J = 9.0 Hz, 1 H), 4.55 (m, 1 H), 3.46 (s, 3 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.32 (s, 3 H), 2.98 (m, 2 H), 2.41 (m, 1 H), 1.99 (m, 1 H), 1.87 (m, 1 H), 1.76 (m, 1 H), 1.30 (d, J = 6.3 Hz, 3 H), 1.11 (p, J = 11.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 285.2 (t, J = 6.3 Hz), 283.5 (t, J = 5.8 Hz), 175.8, 175.5, 167.3, 166.6, 156.0 (m), 154.7, 152.4, 150.2 (t, J = 9.8 Hz), 135.1 (br), 130.7, 129.8 (d, J = 24.4 Hz), 129.4 (d, J = 23.9 Hz), 127.9 (br), 100.1, 88.5, 58.9, 58.8, 51.1, 50.9, 50.8, 50.6, 28.7, 21.4, 19.6; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −7.83 (s), −7.80 (s); IR (CH_2Cl_2) 1717 (s), 1692 (s), cm^{-1}; MS(FAB) m/e calcd for $C_{57}H_{56}O_{10}P_2IrBF_4$ − BF_4 1155.2978, obsd 1155.2948. Anal. Calcd for $C_{57}H_{56}O_{10}P_2IrBF_4 \cdot {}^1/_3Et_2O$: C, 55.31; H, 4.72. Found: C, 54.99; H, 5.10.

Reaction of 8 and Pyridine. Formation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(=O)CH$_2$CH$_2$CH$_2$NC$_5$H$_5$]$^+$BF$_4^-$ (14, R = CO$_2$CH$_3$). To a methylene chloride solution (25 mL) of **8** (150 mg, 0.131 mmol, 51 mM) was added by syringe pyridine (200 μL, 2.5 mmol). The solution was stirred at 23 °C for ~12 h and concentrated on a rotary evaporator; hexanes were added to give **14** (166 mg, 0.13 mmol, 99%) as an off-white solid: ^{1}H NMR ($CDCl_3$) δ 8.39 (d, J = 5.9 Hz, 2 H, N=C*H*CH=), 8.36 (t, J = 7.9 Hz, 1 H, N=CHCH=C*H*), 7.93 (t, J = 7.0 Hz, 2 H, N=CHC*H*=CH), 7.3–7.5 (m, 2 PPh$_3$), 3.80 (t, J = 8.1 Hz, 2 H, C*H*$_2$N), 3.56 (s, 3 H, CO$_2$C*H*$_3$), 3.45 (s, 3 H, CO$_2$C*H*$_3$), 3.30 (s, 3 H, CO$_2$C*H*$_3$), 3.24 (s, 3 H, CO$_2$C*H*$_3$), 1.97 (t, J = 6.7 Hz, 2 H, COC*H*$_2$), 1.20 (p, J = 7.3 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 229.5 (t, J = 6.7 Hz), 175.6 (t, J = 8.1 Hz), 173.8, 173.1, 168.2, 166.0 (t, J = 11.2 Hz), 165.1, 156.4, 148.2, 148.1 (t, J = 9.7 Hz), 145.3, 144.0, 134.7 (t, $J_{PC+P'C}$ = 10.1 Hz), 130.6, 129.6 (t, $J_{PC+P'C}$, = 57.7 Hz), 128.5, 127.7 (t, $J_{PC+P'C}$, = 10.2 Hz), 61.5, 60.5, 51.0, 50.8, 50.6, 50.4, 27.8; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −12.46; IR (CH_2Cl_2) 2025 (s), 1710 (s), 1625 (m) cm^{-1}; MS(FAB), m/e calcd for $C_{58}H_{53}NO_{10}P_2IrBF_4$ − BF_4 1178.2774, obsd 1178.2753. Anal. Calcd for $C_{58}H_{53}NO_{10}P_2IrBF_4$: C, 55.08; H, 4.23; N, 1.11. Found: C, 55.35; H, 4.30; N, 1.08.

Reaction of 8 and PMe$_3$. Formation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C=CHCH$_2$CH$_2$O] (15, R = CO$_2$CH$_3$). A 25-mL round-bottom flask equipped with a magnetic stir bar was charged with **8** (146 mg, 0.12 mmol, 12 mM) and 10 mL of acetone, and the solution was cooled to −76 °C. PMe_3 (14.7 mg, 0.19 mmol) was vacuum transferred in and the solution was stirred at 23 °C for 3 h. Hexanes were then added and the slurry was filtered in an efficient hood to afford **15** (138 mg, 0.12 mmol, 100%) as a pink crystalline solid: mp (sealed capillary) 107–109 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.2–7.5 (m, 2 PPh$_3$), 4.39 (br s, 1 H, =C*H*), 3.87 (t, J = .5 Hz, 2 H, C*H*$_2$O), 3.48 (s, 3 H, CO$_2$C*H*$_3$), 3.35 (s, 3 H, CO$_2$C*H*$_3$), 3.13 (s, 3 H, CO$_2$C*H*$_3$), 3.06 (s, 3 H, CO$_2$C*H*$_3$), 2.36 (t, br, J = 9.4 Hz, 2 H, C*H*$_2$CH$_2$O); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 174.3, 173.8 (t, J = 8.6 Hz), 172.5, 169.9, 165.6, 165.2, 155.0, 151.7, 149.5, 147.0 (t, J = 9.8 Hz), 135.2 (t, $J_{PC+P'C}$ = 8.0 Hz), 131.6 t, $J_{PC+P'C}$ = 57.6 Hz), 130.3, 127.5 (t, $J_{PC+P'C}$, = 8.5 Hz), 109.5, 69.7, 51.1, 50.9, 50.1, 50.0, 31.9; ^{31}P{^{1}H} NMR (CD_3NO_2) δ −15.7 (s); IR (CH_2Cl_2) 2048 (vs), 1713 (vs) cm^{-1}; MS(FAB), m/e calcd for $C_{53}H_{47}O_{10}P_2Ir$ + H^+ 1099.2352, obsd 1099.2379. Anal. Calcd for $C_{53}H_{47}O_{10}P_2Ir$: C, 57.97; H, 4.31; P, 5.64. Found: C, 57.98; H, 4.52; P, 5.70.

Conversion of 15 to 14. An NMR tube was charged with **15** (0.004 mmol, ~10 mM), $C_5H_5NH^+BF_4^-$ (0.04 mmol), and CD_3CN. The tube was sealed and the solution monitored by ^{1}H NMR spectroscopy. Initially a rapid conversion of **15** to carbene complex **8** occurred, followed by a slow (days) conversion of **8** to **14**.

Reaction of 8 and PPh$_3$. Formation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(=O)CH$_2$CH$_2$CH$_2$PPh$_3$]$^+$BF$_4^-$ (16, R = CO$_2$CH$_3$). An NMR tube was charged with a chloroform-d_1 solution (0.51 mL) of **8** (36.5 mg, 0.031 mmol, 60 mM) and PPh_3 (15.6 mg, 0.06 mmol). The tube was sealed under partial vacuum and the solution was heated at 49 °C for ~35 h. ^{1}H NMR spectroscopy on the sample indicated formation of **16** in 87% yield. The tube was opened, the volatiles were evaporated under vacuum, and the residue was recrystallized from chloroform/diethyl ether to give **16** as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.1–7.8 (m, 3 PPh$_3$), 3.63 (s, 3 H, CO$_2$C*H*$_3$), 3.41 (s, 3 H, CO$_2$C*H*$_3$), 3.20 (s, 3 H, CO$_2$C*H*$_3$), 3.19 (s, 3 H, CO$_2$C*H*$_3$), 2.42 (m, br, 4 H, C*H*$_2$CH$_2$C*H*$_2$), 0.89 (m, br, 2 H, CH$_2$C*H*$_2$CH$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 232.0 (t, J = 6.8 Hz), 176.0, 175.1 (t, J = 8.7 Hz), 174.1, 167.8, 165.3, 165.2, 155.5, 150.0 (t, J = 8.9 Hz), 147.8, 134.8 (br), 133.7 (br), 130.4 (br), 129.2 (t, $J_{PC+P'C}$ = 57.8 Hz), 127.5 (br), 118.1 (d, J = 85.5 Hz), 64.9 (d, J = 13.6 Hz), 50.8, 50.5, 50.3, 21.1 (d, J = 50.0 Hz), 18.8; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −11.9, 25.1; IR (CH_2Cl_2) 1986 (s), 1718 (br s), 1622 (m) cm^{-1}; MS(FAB), m/e calcd for $C_{71}H_{63}O_{10}P_3Ir$ + H^+ 1362.3342, obsd 1362.3407.

Reaction of 9 and Pyridine. Formation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C(C=O)CH$_2$CH$_2$CH(CH$_3$)NC$_5$H$_5$]$^+$BF$_4^-$ (17, R = CO$_2$CH$_3$). A round-bottom flask was charged with **9** (164 mg, 0.14 mmol, 9 mM), pyridine (1 mL, 12 mmol), and chloroform (15 mL), and the solution was refluxed for 12 h. Removal of the volatiles by rotary evaporation and recrystallization of the residue from THF/hexanes gave **17** (110 mg, 0.086 mmol, 63%) as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 8.46 (d, J = 6.0 Hz, 2 H, N=C*H*CH=), 8.38 (t, J = 7.7 Hz, 2 H, N=CHCH=C*H*), 7.95 (t, J = 6.9 Hz, 2 H, N=CHC*H*=CH), 7.3–7.6 (m, 2 PPh$_3$), 3.94 (m, 1 H, C*H*CH$_3$), 3.55 (s, 3 H, CO$_2$C*H*$_3$), 3.45 (s, 3 H, CO$_2$C*H*$_3$), 3.31 (s, 3 H, CO$_2$C*H*$_3$), 3.24 (s, 3 H, CO$_2$C*H*$_3$), 1.91 (m, 1 H, COC*H*$_2$), 1.67 (m, 1 H, COC*H*$_2$), 1.23 (m, 5 H, CH$_2$C*H*$_2$CHC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 229.1 (t, J = 6.8 Hz), 175.6, 175.7, 173.8, 168.3, 166.6 (m), 165.2, 165.0, 156.7, 148.1 (m), 147.4 (t, J = 8.7 Hz), 142.4, 134.8 (t, J = 5.0 Hz), 130.7, 130.0, 129.7 (t, J = 29 Hz), 129.6 (t, J = 29 Hz), 128.7, 127.7 (q, J = 4.8 Hz), 69.3, 60.7, 51.1, 50.9, 50.6, 50.5, 33.4, 20.2; IR (CH_2Cl_2) 2045 (s), 1773 (s), 1710 (br, vs), 1630 (m) cm^{-1}; MS(FAB), m/e calcd for $C_{59}H_{55}NO_{10}P_2Ir$ BF_4 − BF_4 1192.2928, obsd 1192.2931.

Reaction of 9 and Pyridine. Formation of Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)[C=CHCH$_2$CHCH$_3$O] (18, R = CO$_2$CH$_3$). Addition of pyridine (0.5 mL, 6.2 mmol) to a benzene solution (10 mL) of **9** (630 mg, 0.53 mmol, 53 mM) led to immediate precipitation of a white solid. The mixture was filtered through silica gel, the solvent removed by rotary evaporation, and the remaining yellow solid washed with hexanes to give **18** (520 mg, 0.47 mmol, 88%): ^{1}H NMR ($CDCl_3$) δ 7.2–7.6 (m, 30 H, 2 PPh$_3$), 4.41 (s, br, 1 H, =C*H*), 4.12 (m, 1 H, C*H*CH$_3$), 3.50 (s, 3 H, CO$_2$C*H*$_3$), 3.40 (s, 3 H, CO$_2$C*H*$_3$), 3.18 (s, 3 H, CO$_2$C*H*$_3$), 3.09 (s, 3 H, CO$_2$C*H*$_3$), 2.48 (t, J = 12.3 Hz, 1 H, C*H*$_2$), 2.02 (t, J = 12.3 Hz, 1 H, C*H*$_2$), 1.18 (d, J = 6.0 Hz, 3 H, CHC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 173.7, 172.9 (t, J = 8.9 Hz), 172.3, 169.2, 165.5, 162.3 (t, J = 11.0 Hz), 153.6, 152.9 (t, J = 7.1 Hz), 149.8, 146.3 (dt, J = 2.0, 9.0 Hz), 134.7 (br), 131.7 (heptet), 129.7 (br), 126.9 (br), 109.44, 109.41, 50.7, 505.5, 49.8, 39.4, 21.7; IR (CH_2Cl_2) 2141 (vs), 1700 (vs), 1577 (w) cm^{-1}; MS(FAB), m/e calcd for $C_{54}O_{49}O_{10}P_2Ir$ + H (isotope of lowest atomic weight) 1111.2490, obsd 1111.2568.

Reaction of 12 and CH$_3$NH$_2$. Conversion to Ir(CR=CRCR=CR)(PPh$_3$)$_2$(H)(NH$_2$CH$_3$) (19, R = CO$_2$CH$_3$) and 2-(2(5*H*)-furanylidene)-tetrahydrofuran (20). A 25-mL round-bottom flask equipped with a stir bar was charged with **12** (1.08 g, 0.88 mmol, 88 mM) and 10 mL of dry chloroform and cooled to −76 °C. Methylamine gas was distilled in under vacuum and the solution was warmed to 23 °C and stirred under nitrogen for ~10 h. The solvent and excess amine were removed under vacuum and the air-sensitive 2-(2(5*H*)-furanylidene)tetrahydrofuran (**20**; 112 mg, 0.81 mmol, 92%) was distilled from the flask by heating the oily residue at 65 °C (0.01 mmHg). Chloroform was added to the flask and the insoluble methyl ammonium tetrafluoroborate (101 mg, 0.85 mmol, 97%) was removed by filtration. Evaporation of the chloroform washings gave iridium hydride **19** (900 mg, 0.87 mmol, 99%).

20: ^{1}H NMR ($CDCl_3$) δ 6.43 (dt, J = 6.2, 2.3 Hz, 1 H, C*H*=CHCH$_2$), 5.86 (m, 1 H, =C*H*), 4.93 (p, J = 2.3 Hz, 2 H, CH=CHC*H*$_2$), 4.02 (t, J = 6.7 Hz, 2 H, OC*H*$_2$CH$_2$), 2.62 (br, tt, J = 7.4, 2.2 Hz, 2 H, OCH$_2$CH$_2$C*H*$_2$), 2.01 (p, J = 7.2 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 140.3, 133.4, 124.4, 122.1, 76.6, 70.3, 25.4, 25.3; ^{13}C NMR ($CDCl_3$) δ 140.3 (m), 133.4, (m) 124.4 (dm, J = 174 Hz), 122.1 (dm, J = 174 Hz), 76.59 (tdd, J = 149.0, 12.0, 12.2 Hz), 70.3 (tm, J = 150 Hz), 25.36 tm, J = 177 Hz), 25.3 (tm, J = 177 Hz); IR (CH_2Cl_2) 2950 (m), 2875 (s), 2850 (s), 1774 (m), 1713 (m), 1450 nw) cm^{-1}; MS(EI), m/e (relative intensity) 138 (M^+, 87), 110 (M^+ − 28, 72), 95 (M^+ − 43, 100).

The assigned structure of **20** was supported by ^{1}H NMR ($CDCl_3$) spectroscopy decoupling experiments. Irradiation of the 2.62 ppm resonance resulted in the following multiplicity changes: δ 4.93 (p to t, J = 2.1 Hz), 2.01 (p to t, J = 6.6 Hz) 4.02 (t, no change), 5.85 (m to dt, J = 6.2, 2.4 Hz)8, 6.43 (dt, no change). Irradiation of the 4.93 ppm resonance resulted in the following multiplicity changes: δ 2.01 (p, no change), 2.62 (br tt to a br t, J = 7.5 Hz), 5.85 (m to br d, J = 6.0 Hz), 6.43 (dt to d, J = 6.1 Hz).

19: mp (sealed capillary) 179–181 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.2–7.6 (m, 30 H), 3.57 (s, 3 H), 3.38 (s, 3 H), 3.17 (s, 3 H), 2.87 (s, 3 H), 1.71 (br, 2 H), 1.29 (t, J = 12.6 Hz, 3 H), −10.6 (t, J = 11 Hz, 1 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 177.5, 176.1, 168.6, 165.5, 155.0 (t, J = 8.6 Hz), 150.3, 145.8, 134.3 (br), 130.4 (t, $J_{PC+P'C}$ = 52.5 Hz), 129.6, 128.2, 127.6 (br), 50.6, 50.4, 50.1, 49.8, 38.4; IR (THF) 2030 (m), 1670 (s), 1710 (vs) cm^{-1}; MS(FAB), m/z calcd for $C_{49}H_{48}O_8N_2Ir$ (isotope of lowest mass) 1031.2461, obsd 1031.2443. Anal. Calcd for $C_{49}H_{48}NO_8P_2Ir \cdot {}^1/_3C_6H_6$: C, 58.32; H, 4.83. Found: C, 58.13; H, 4.80. The sample sent out for elemental analysis was recrystallized from methylene chloride/pentane and then dissolved in C_6H_6, followed by

evaporation of the solvent to remove traces of CH_2Cl_2 and pentane. Integration of the phenyl region in a ^1H NMR spectrum of the sample was consistent with the presence of $^1/_3C_6H_6$.

Conversion of 20 to 21 in the Air. In the drybox, an NMR tube was charged with **20** (21 mg, 0.15 mmol, 0.38 M) and chloroform-d_1 (0.40 mL). After an initial ^1H NMR spectrum of the sample, which indicated pure **20**, the tube was exposed to the air. Within 6.5 h **20** had decomposed completely to give a 64% yield of **21** as determined by ^1H NMR spectroscopy. The solution was concentrated under vacuum, loaded onto a short column of silica gel, and eluted, first with chloroform (to remove uncharacterized impurities) and then with ethyl acetate. The ethyl acetate washings were evaporated under vacuum to give **21** as a yellow oil, judged to be pure by ^1H NMR spectroscopy: ^1H NMR ($CDCl_3$) δ 7.56 (br, 1 H, C*H*=), 7.19 (d, J = 3.5 Hz, 1 H, C*H*=), 6.52 (dd, J = 3.5, 1.2 Hz, 1 H, C*H*=), 3.71 (t, J = 6.1 Hz, 2 H, CH_2O), 2.97 (t, J = 6.1 Hz, 2 H, $CH_2C(O)$), 1.97 (p, J = 6.4 Hz, 2 H, $CH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 189.6, 152.5, 146.4, 117.2, 112.1, 62.0, 35.0, 26.7; MS(EI), m/z calcd for $C_8H_{10}O_3$ 154.0624, obsd 154.0699.

Conversion of 12 to Ir(CR=CRCR=CR)(PPh$_3$)$_2$(H)(NC$_5$H$_5$), (22, R = CO$_2$CH$_3$). An NMR tube was charged with **12** (6.5 mg, 0.005 mmol, 13 mM), nitrobenzene-d_5 (0.4 mL), and pyridine (2 μL, 0.025 mmol). The tube was sealed under nitrogen and the solution was periodically monitored by ^1H NMR spectroscopy. After 20 h at 55 °C, **12** was converted to **20** (50%) and a new iridium hydride species, **22** (46%), in addition to a number of unidentified minor products. Complex **22** was independently synthesized from hydride **19** and pyridine as follows: A 25-mL round-bottom flask equipped with a stir bar was charged with **19** (220 mg, 0.21 mmol, 35 mM), chloroform (6 mL), and pyridine (400 μL, 5.0 mmol). The solution was stirred at 23 °C for 3 days. The volatiles were removed by rotary evaporation and the residue extracted with benzene. Evaporation of the benzene led to **22** (207 mg, 0.19 mmol, 90%) as a yellow solid: ^1H NMR ($CDCl_3$) δ 7.98 (br, 2 H), 6.9–7.4 (m, ~31 H), 6.03 (br, 2 H), 3.57 (s, 3 H), 3.30 (s, 3 H), 3.11 (s, 3 H), 2.96 (s, 3 H), −10.46 (t, J = 16 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 180.3, 175.7, 167.1, 166.2, 161.0 (m), 147.6, 143.6, 141.1 (t, J = 10 Hz), 134.5 (t, J_{PC+PC} = 11 Hz), 134.0, 130.9 (t, J_{PC+PC} = 54 Hz), 129.0 (br), 128.3, 127.0 (t, J_{PC+PC} = 10 Hz), 124.3, 60.2, 50.1, 50.0, 49.9; IR (CH_2Cl_2) 2040 (w), 1690 (s, br) cm^{-1}; MS(FAB), m/e (relative intensity) 1001 (M^+ − H − NC_5H_5, 45), 942 (M^+ − H − NC_5H_5 − CO_2Me, 15).

Conversion of 12 to 12-d_4 and Subsequent Reaction with CH_3ND_2. A 25-mL round-bottom flask equipped with a stir bar was charged with bis(carbene) **12** (143 mg, 0.12 mmol, 7.8 mM), chloroform (15 mL), and D_2O (2 mL). The two-phase mixture was stirred at 23 °C for 19 h. An aliquot of the solution was removed from the flask to an NMR tube. The solvent was evaported under vacuum and chloroform-d_1 distilled into the tube. A ^1H NMR spectrum of the sample indicated complete conversion to **12-d_4**.

To an NMR tube containing a chloroform-d_1 solution of **12-d_4** (9.1 mg, 0.007 mmol, 16 mM) was added a preequilibrated mixture of D_2O (0.17 mL) and 40% (aqueous, 15 μL) CH_3NH_2. At 23 °C complete conversion to **19-d_2** and **20-d_3** was observed by ^1H NMR spectroscopy.

Reaction of 13 and CH_3NH_2. Conversion to Iridium Hydride 19, 2-(2(5-Methyl)furanylidene)tetrahydrofuran (25), and 2-(2(5*H*)-Furanylidene)-5-methyltetrahydrofuran (24). A 25-mL round-bottom flask equipped with a stir bar was charged with **13** (400 mg, 0.32 mmol) and 7 mL of dry chloroform and cooled to −76 °C. Methylamine gas (1.6 mmol) was distilled in under vacuum and the solution was warmed to room temperature. After 5 min, the solution was cooled to 0 °C and the solvent removed under vacuum. The residue was then heated at 60 °C (0.005 mmHg) and the clear distillate collected and analyzed by ^1H NMR spectroscopy and GC–MS. The ^1H NMR spectrum indicated a 59:41 ratio of **25** to **24**.

24: ^1H NMR (CD_2Cl_2) δ 6.39 (dt, J = 6.0 Hz, 2.3 Hz, 1 H), 5.84 (m, 1 H), 4.90 (p, J = 2.3 Hz, 2 H), 4.24 (m, 1 H), 2.62 (m, 1 H), 2.10 (m, 2 H), 1.58 (m, 1 H)8 1.26 (d, J = 6 Hz, 3 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 20.6, 26.2, 32.7, 76.8, 78.4, 122.4, 124.6, and two of the following: 132.7, 132.9, 139.1, 139.5.

25: ^1H NMR (CD_2Cl_2) δ 6.35 (dd, J = 6.3 Hz, 2.0 Hz, 1 H), 5.77 (br d, J = 5.7 Hz, 1 H), 5.18 (m, 1 H), 3.99 (t, J = 6.6 Hz, 2 H), 2.57 (br t, J = 6.4 Hz), 1.99 (p, J = 7.2 Hz, 2 H), 1.27 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (CD_2Cl_2) δ 21.7, 25.8, 25.6, 70.6, 83.7, 121.7, 129.9, and two of the following: 132.7, 132.9, 139.1, 139.5. Both the ^1H and ^{13}C NMR assignments for **24** and **25** are by comparison with **20**.

X-ray Structure Determinations for 8 and 12. Crystallographic data are summarized in Table II. Specimens for both which were found satisfactory for diffraction studies were mounted on glass fibers. Both photographic and diffraction data were used in the assignment of space groups. For **8**, the lack of suitable symmetry for the monoclinic centrosymmetric space group $C2/c$ initially suggested that the correct space group was Cc; subsequent solution and refinement results confirmed the appropriateness of this choice. For **12**, the centrosymmetric triclinic space group $P\bar{1}$ was assumed correct throughout; the chemical reasonableness of the results support these choices.

Data were collected with a Nicolet R3m/μ diffractometer at the University of Delaware. The variation in the intensities of 3 standard reflections was less than 1% in both cases.

The structures were solved by Patterson syntheses and completed by subsequent difference Fourier syntheses. In **12** a molecule of the recrystallization solvent, $CHCl_3$, was found in the lattice for each ionic formula. All non-hydrogen atoms were treated as idealized isotropic contributions. In both structures phenyl rings were constrained to rigid planar hexagons (dCC = 1.395 Å) and the BF_4^- counterions were constrained to rigid tetrahedra (dBF = 1.34 Å).

All software is contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). The supplementary materials have been deposited with the previously published communications.[8a,f]

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