Activation of Aliphatic Ethers by $Tp^{Me2}Ir$ Compounds: Multiple C−H Bond Activation and C−C Bond Formation

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Benzene solutions of the unsaturated fragment $Tp^{Me2}Ir(C_6H_5)_2$ (**1**), generated *in situ* from either $Tp^{Me2}Ir(C_2H_4)_2$ or $Tp^{Me2}Ir(C_6H_5)_2(N_2)$, react with methyl ethers $MeOBu^t$, $MeOBu^n$, and $MeOCH_2CH_2OMe$ to give the organometallic hydride carbene products $Tp^{Me2}(H)_2(=C(H)OR)$ **4** (R = Bu^t, **4a**; Bu^n, **4b**; CH_2CH_2OMe, **4c**) along with benzylic ethers $C_6H_5CH_2OR$ **5**. The overall reaction is very complex and involves the participation of two molecules of the ether, MeOR, and one of benzene per molecule of the iridium precursor. The latter induces multiple C−H bond cleavage along with the formation of a new C−C bond. Hydride carbenes of composition $Tp^{Me2}Ir(H)(C_6H_5)(=C(H)OR)$ (**2**) are early intermediates of this reaction. They can be shown to undergo a reversible 1,2-H shift between the metal atom and the carbene carbon atom, until eventually β-H elimination from the Ir−C_6H_5 unit allows the C−C coupling through a nonisolable benzyne intermediate. Me−OR bond cleavage, although somewhat more energetically demanding than C−H activation, can also occur and has been demonstrated in the reaction of **1** with Me−OBu^n, which permits the isolation of the hydride *n*-propyl carbonyl complex $Tp^{Me2}Ir(H)(CH_2CH_2CH_3)(CO)$, **10b**.

Introduction

One of the main areas of study of modern organometallic chemistry deals with the selective formation and cleavage of the bonds formed by carbon with other common atoms such as hydrogen, oxygen, nitrogen, or carbon itself. In particular, transition metal compounds capable of inducing C−H bond activation and subsequent C−C bond formation have important applications in the synthesis of complex organic molecules from simple, commonly available substrates.[1,2]

In the last years, transition metal chemistry has provided numerous examples of C−H[2] and other C−X bond activation reactions (X = F, O, N, etc.).[3] An important class of organic molecules intensively investigated for C−H bond functionalization, i.e., C−H bond activation and subsequent C−C or C−X bond formation, is that formed by saturated hydrocarbons, as these substances are major components of natural gas and petroleum. However, despite this continuous attention, at present these substances cannot be used as raw materials for practical, large-scale catalytic processes that would convert them into valuable products.[4,5] The reasons for this are both kinetic and thermodynamic in nature. For example, the conversion of a saturated hydrocarbon such as CH_4 into a highly reactive $M{=}CH_2$ unit (that could then be transformed into useful products) plus dihydrogen (Scheme 1a) is a very endothermic process[6] that faces in addition the kinetic difficulty of bringing the C−H bond to be broken into close proximity with the metal atom. There is actually very little incentive for this approach, since the interaction of the metal atom with the C−H bond in the putative alkane complex intermediate (**A**, Scheme 1b) is expected to be very weak. However, for an ether or amine substrate, coordination of the oxygen or nitrogen atom facilitates this approach (structure **B**), and if a suitable chemical sink is provided for the abstracted hydrogen atoms (for instance the formation of a strong C−H bond with a sacrificial, coordinated alkyl or aryl group; see below), the double C−H bond cleavage reaction may become thermodynamically allowed.

Considering as a way of an example the activation of a methyl ether MeOR (Scheme 1c), the initial C−H bond activation step can be assisted thermodynamically by the formation of a strong C−H bond with the leaving alkyl or aryl group (R′ in Scheme 1c), and if the metal is able to form a sufficiently strong M−H bond, the resulting metal−alkoxymethyl derivative **C** can evolve further by means of an α-H elimination to yield a hydride Fischer carbene product **D**. Nonetheless, an intermediate like

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(1) (a) *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999. (b) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (c) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698.

(2) (a) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *46*, 223. (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (c) Blackmore, I. J.; Jin, X.; Legzdins, P. *Organometallics* **2005**, *24*, 4088.

(3) For some selected papers see: (a) Brown, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749. (b) Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183. (c) Yamamoto, A. *Adv. Organomet. Chem.* **1992**, *34*, 111.

(4) *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous, and Industrial Catalysis*; Moulijn, J. A., van Leeuwen, P. W. N. M., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1993.

(5) For representative examples of catalytic C−H bond functionalization see: (a) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (b) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992. (c) Periana, R.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814.

(6) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

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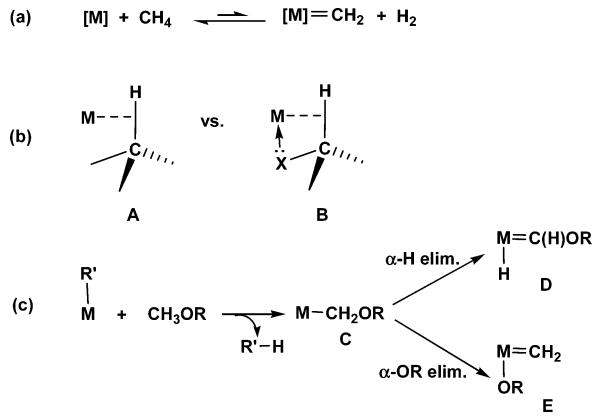
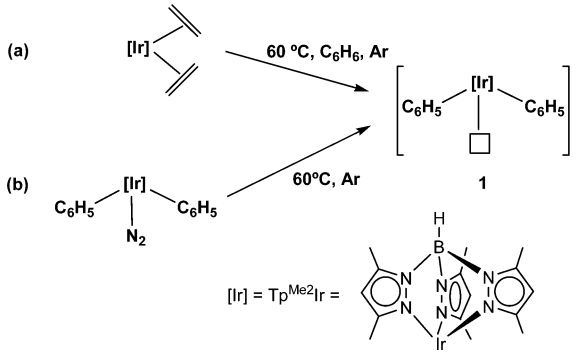
Scheme 1



C can also experience an alternative decomposition pathway, namely, α-alkoxy elimination to afford a metal−alkoxy−methylene complex **E**. This sequence of steps represents an attractive, albeit little explored, reactivity mode, as it provides a simple, straightforward route for the cleavage of unstrained C−O bonds. Despite the importance of this bond cleavage reaction, relevant to the hydrodeoxygenation of crude oil,[7] few unequivocal examples have been provided and mechanistic information is scarce.[8−11]

Following prior work from our laboratory on the activation of cyclic ethers by $Tp^{Me2}Ir$ compounds (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate),[12] we have studied the reactivity of aliphatic ethers that contain one methyl terminus, MeOR (R = CMe_3, $CH_2CH_2CH_2CH_3$, CH_2CH_2OMe), toward the Lewis acid organometallic fragment $Tp^{Me2}Ir(C_6H_5)_2$, generated *in situ* in the presence of the ether. Herein we provide full details of the complex chemical reactivity that ensues, which leads initially to Fischer-type carbenes as a result of a regioselective double C−H sp^3 activation of the Me group adjacent to the ether oxygen atom. Under somewhat more forcing conditions and using C_6H_6 as the reaction solvent, a C−C coupling between one molecule of the ether and one of C_6H_6 (each having experienced previously the cleavage of a C−H bond) is observed. Finally, for some of the compounds investigated the rupture of one of the C−O bonds of the ether has also been ascertained. Part of this work has appeared in preliminary form.[13]

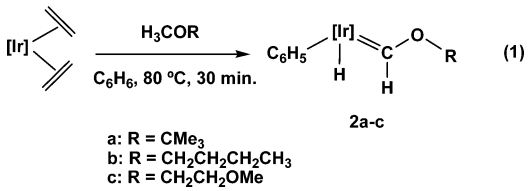
Scheme 2



Results and Discussion

Fischer-Type Carbenes by Double C−H Bond Activation of Methyl Ethers. As briefly mentioned, we have studied the reactivity of the methyl ethers $MeOCMe_3$ ($MeOBu^t$), $MeOC_4H_9$ ($MeOBu^n$), and $MeOCH_2CH_2OMe$ (dme, 1,2-dimethoxyethane) toward the unsaturated frament $Tp^{Me2}Ir(C_6H_5)_2$ (**1**), which may be generated *in situ* by either of the procedures shown in Scheme 2. While experimentally the use of the bis(ethene) precursor $Tp^{Me2}Ir(C_2H_4)_2$ is advisable (Scheme 2a) and avoids prior isolation of the dinitrogen complex $Tp^{Me2}Ir(C_6H_5)_2(N_2)$, in other cases, particularly for ^1H NMR monitoring of reaction mixtures and for other mechanistic studies, employing the dinitrogen complex becomes mandatory. Both methods prove convenient for all reactions investigated and provide essentially identical results. For the sake of simplicity, in the following equations and schemes the unsaturated iridium fragment **1**, generated by either of these procedures, will be represented as the iridium complex precursor.

Heating a benzene solution of **1** with $MeOBu^t$ (5 equiv, an excess) at 80 °C under argon (eq 1) gives rise to the Fischer-type carbene complex **2a** in spectroscopic yield higher than 95%. The analogous reactions between **1** and $MeOBu^n$ and dme yield the related hydride carbenes **2b** and **2c**, respectively.



(1)

Compounds **2** can be readily characterized by spectroscopic methods. A sharp, medium-intensity IR absorption at ca. 2140 cm^{-1} and a high-field ^1H NMR resonance between δ −16.4 and −17.3 ppm are diagnostic for the existence of a hydride functionality in the molecules of complexes **2**. In turn, the carbene C(H)OR unit is responsible for strongly deshielded ^1H and $^{13}C\{^1H\}$ NMR resonances. The former is located around 15 ppm, while the carbene ^{13}C nuclei of **2** resonate in the chemical shift range between 253 and 263 ppm. Restricted rotation around the iridium−carbene bond, possibly of steric rather than electronic origin, manifests in the observation at low temperatures of two carbene rotamers for the dme-derived compound **2c** (coalescence temperature −45 °C). Similarly, for **2a** and **2b** the ^1H resonances due to the Ir−*H* and Ir−C(*H*)OR groups are broad at room temperature, indicating somewhat slow rotamer equilibria under these conditions.

The nature of the carbene ligand of compounds **2**, Ir=C(H)-OR, clearly demonstrates that similarly to previously reported

(7) (a) Caldwell, T. E.; Abdelrehim, I. M.; Land, D. P. *J. Am. Chem. Soc.* **1996**, *118*, 907. (b) Furimsky, E. *Catal. Rev. Sci. Eng.* **1983**, *25*, 421.

(8) (a) Weissman, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2004**, *23*, 3931. (b) Van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.

(9) (a) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409. (b) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132. (c) Van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Vigalok, A.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 625. (d) Chataui, N.; Tatamidani, H.; Ie, Y.; Kakinchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 4849. (e) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1996**, *15*, 2860. (f) Mayer, J. M. *Polyhedron* **1995**, *14*, 3273.

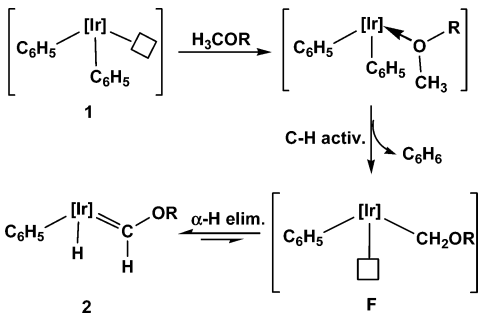
(10) (a) Lin, Y.-S.; Yamamoto, A. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 161−192. (b) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L-Ch.; Schrock. R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742. (d) Yamamoto, Y.; Sato, R.; Matsuo, F.; Sudoh, C.; Igoshi, T. *Inorg. Chem.* **1996**, *35*, 2329. (e) Empsall, H. D.; Hyde, E. M.; Jones, C. H.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1980.

(11) Lara, P.; Paneque, M.; Poveda, M. L.; Salazar, V.; Santos, L. L.; Carmona, E. *J. Am. Chem. Soc.* **2006**, *128*, 3512.

(12) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Carmona, E. *Chem.−Eur. J.* **1998**, *4*, 2225.

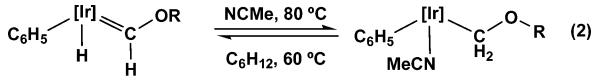
(13) Paneque, M.; Poveda, M. L.; Santos, L. L.; Salazar, V.; Carmona. E. *Chem. Commun.* **2004**, 1838.

Scheme 3



studies[12,14] the Tp′Ir(III) fragment (Tp′ is a general representation of hydrotris(pyrazolyl)borate ligands, with different pyrazolyl substituents) induces the regioselective activation of two C−H bonds in α-position with respect to the ether functionality. Interestingly, despite the significantly higher statistic probability for C−H bond activation of the Me groups of the Bu^t fragment of MeOBu^t, the corresponding alkylidene complex cannot be detected; only the Fischer-type carbene **2a** appears to form. This clearly reflects the need of iridium coordination to the ether (structure **B** of Scheme 1b) for the C−H bond activation to occur in an effective manner. For MeOBu^n and dme cleavage of the somewhat weaker $-OCH_2-$ bonds is not detected. While this may be partly due to the higher steric hindrance associated with the methylene C−H bond activation in comparison with the methyl C−H bond cleavage, it is also possible that as found for other C−H bond activations the cleavage of the stronger primary $-CH_3$ bonds is thermodynamically more favorable than that of the secondary $-OCH_2-$ bonds, due to the greater strength of the resulting metal−primary carbon bond.[15]

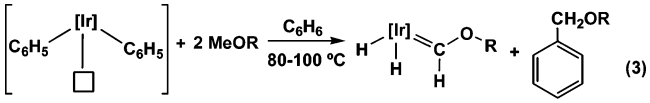
Scheme 3 shows a plausible reaction pathway for the conversion of **1** into **2** by action of the methyl ethers MeOR (R = Bu^t, Bu^n, OCH_2CH_2OMe). The first C−H bond cleavage results in the elimination of benzene by formation of a very strong C_6H_5−H bond (110 kcal mol^{-1}).[6,16] Considering the strong tendency of Tp^{Me2}Ir(III) complexes to adopt a six-coordinated octahedral geometry, it is likely that benzene elimination occurs in a concerted manner, rather than by an oxidative addition/reductive elimination sequence of reaction steps. This hypothesis is in accord with results reported for somewhat related systems,[17] and it is further supported by theoretical calculations on the activation of methyl aryl ethers by the same Tp^{Me2}Ir(C_6H_5)$_2$ fragment (e.g., anisole and methyl-substituted anisoles[11]) that are presently under way and will be reported in due course. The resulting alkoxymethyl intermediate species (analogous to intermediate **C** of Scheme 1c) converts into the hydride carbene product by means of an α-H elimination reaction. It is worth remarking that the α-H elimination is reversible. As discussed below, intermediates **F** can be trapped in the form of the corresponding NCMe adducts **3** (*vide infra*), which undergo thermal decomposition to the hydride carbenes **2** (eq 2). Examples of reversible 1,2-H shifts, although known, are still rare.[18] However, in addition to the **F** ⇌ **2** equilibrium of Scheme 3, and eq 2, we have found a number of reversible α-H elimination reactions in our studies on the migratory insertion reactions of iridium carbenes.[11,13,14c,19]



a: R = CMe_3
b: R = $CH_2CH_2CH_2CH_3$
c: R = CH_2CH_2OMe

Heating acetonitrile solutions of carbenes **2** at 80 °C overnight induces migration of the hydride ligand and allows the isolation of the corresponding adducts **3** (eq 2), which display an IR absorption at ca. 2285 cm^{-1} due to ν(C≡N) of the coordinated molecule of acetonitrile. No evidence for the Ir−H functionality can be found in the IR and the ^{1}H NMR spectra of the compounds. The absence of symmetry in the molecules of **3** is demonstrated by the complexity of their NMR spectra in terms of the number of resonances detected, and in particular by the observation of two resonances between 4.5 and 5.1 ppm ($^2J_{HH}$ ≈ 5 Hz) due to the diastereotopic Ir−CH_2OR protons. As already mentioned and shown also in eq 2, heating cyclohexane solutions of **3** reverts the process and yields back the starting hydride carbenes **2**.

C−H Bond Activation Followed by C−C Bond Forming Reactions. The hydride carbene compounds **2** of eq 1 are only the initial products of the activation of MeOBu^t, MeOBu^n, and dme by the iridium species **1**. Upon prolonged heating at somewhat higher temperatures in the presence of the corresponding ether, further rearrangement occurs, leading to the bis(hydride) carbene complex **4** and to the benzyl ethers **5**. As shown in eq 3, carbenes **2** need not be isolated; the above-mentioned reaction products can be obtained directly from **1** and the respective methyl ether. The crude reaction mixtures contain also minor amounts of some unidentified iridium products. Column chromatography with silica gel permits separation and posterior isolation of **4** and **5**.



a: R = CMe_3
b: R = $CH_2CH_2CH_2CH_3$
c: R = CH_2CH_2OMe

The spectrocopic characterization of the hydride−carbenes **4** is straightforward. Thus, the ^{1}H NMR spectrum of **4a** exhibits a high-field resonance at δ −17.74 due to the two equivalent hydride ligands and a low-field signal at 15.70 ppm (of unit relative intensity, in comparison with two for the hydride ligands) attributed to the carbene proton, C(*H*)OBu^t. The carbene ^{13}C nucleus resonates at 246.9 ppm in the ^{13}C NMR spectrum

(14) (a) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2158. (b) Santos, L. L.; Mereiter, K.; Paneque, M.; Slugovc, C.; Carmona, E. *New J. Chem.* **2003**, *27*, 107. (c) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022. (d) Carmona, E.; Paneque, M.; Santos, L. L.; Salazar, V. *Coord. Chem. Rev.* **2005**, *249*, 1729.

(15) (a) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554. (b) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475.

(16) (a) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *Polyhedron* **1988**, *16/17*, 1429. (b) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(17) (a) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (b) Pittard, K. A.; Lee, J. P.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2004**, *23*, 5514.

(18) (a) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O'Donoghue, M. B.; Davies, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 11876. (b) Lee, D.-H.; Chen, J.; Faller, J. W.; Crabtree, R. H. *Chem. Commun*. **2001**, 213. (c) Clot, E.; Chen, J.; Lee, D.-H.; Sung, S. Y.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H.; Eisenstein, O. *J. Am. Chem. Soc.* **2004**, *126*, 8795.

(19) (a) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *J. Am. Chem. Soc.* **1998**, *120*, 5816. (b) Alías, F. M.; Poveda, M. L.; Sellin, M.; Gutiérrez-Puebla, E.; Monge, A.; Carmona, E. *Organometallics* **1998**, *18*, 4124.

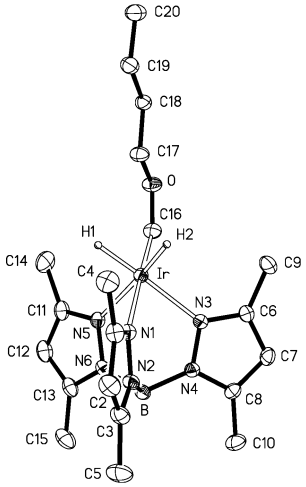
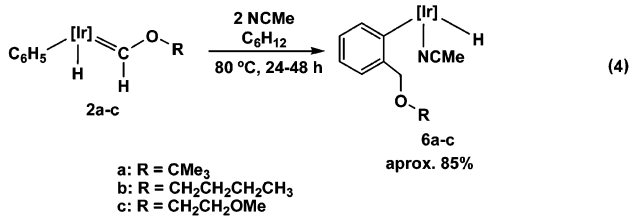


Figure 1. ORTEP view of complex **4b** (hydrogen atoms omitted for clarity except the hydride ligands). Selected bond distances (Å) and angles (deg): Ir−H(1) 1.49(2), Ir−H(2) 1.49(2), Ir−C(16) 1.859(2), Ir−N(1) 2.141(2), Ir−N(5) 2.155(2), Ir−N(3) 2.163(2), C(16)−O 1.326(3), C(17)−O 1.447(3), N(1)−Ir−N(5) 84.8(1), N(1)−Ir−N(3) 83.7(1), N(3)−Ir−N(5) 86.1(1).

and exhibits a $^1J_{CH}$ coupling of 146 Hz. These data are characteristic of a Fischer carbene. The structural complexity of compounds **4** has been confirmed by an X-ray study of **4b**. Figure 1 shows an ORTEP view of the molecules of this compound that includes the atom-numbering scheme and important bond lengths and angles, while Table 1 collects relevant structure data. Only one rotamer is present in the solid state, and this is not the depicted one in eq 3; that is, the OBu^n chain is situated opposing the Tp^{Me2} ligand. The well-known propensity of Tp′ ligands to enforce six-coordinated, octahedrally derived geometries[20] is cleary seen in the structure of the molecules of **4b**, characterized by *trans* angles close to the ideal 180° value (for example C(16)−Ir−N(1) = 178.2(1)°; N(3)−Ir−H(1) = 175.4(11)°) and *cis* angles also similar to the regular 90° value (N−Ir−N for the Tp^{Me2}Ir linkage in the short 84−86° range). The Ir−C(16) bond length to the carbene ligand at 1.859(2) Å is relatively short and indicative of some double-bond character, Ir==C(H)OR. For example, in the cationic species $Ir(H)_2[py\text{-}N(Et)C(Me)(PPh_3)_2]^+$, where little π-back-donation from the Ir(III) center to the carbene carbon can be expected, the $Ir-C_{carbene}$ distance has a value of 2.018 Å, which corresponds to a single Ir−C bond.[18c] In our neutral compounds **4** the moderately good donor properties of the Tp^{Me2} ligand[21] and above all the strong σ-donor capacity of the two hydride ligands result in enhanced π-back-donation to the carbon atom of the carbene ligand. In this regard, comparison with other Ir(III) complexes with π-acceptor ligands is appropriate. For example, the tris(carbonyl) derivative $Ir(SO_3F)_3(CO)_3$ features[22] a ν_{av}(CO) of 2218 cm^{-1}, which is about 75 cm^{-1} higher than that found for gaseous CO (2143 cm^{-1}), while in the mono(carbonyl) derivatives $IrCl_3(CO)(PR_3)_2$ that contain the strongly basic trialkyl phosphines PEt_3[23] or PBu^n_3, ν(CO) appears in the proximity of 2000 cm^{-1}. Finally, the C(16)−O distance within the carbene fragment of **4b** of 1.326(3) Å is short enough to suggest some double-bond character. Accordingly, Ir==C(H)==OR appears to be an adequate electronic description for the iridium−carbene functionality of these complexes.

Doubtless, the reaction depicted in eq 3 that leads to the carbenes **4** and the benzyl ethers **5** represents a complex chemical transformation. To gain information on the nature of the intermediates involved some mechanistic studies have been developed. As already discussed, the carbene compounds **2** react with NCMe at 80 °C to afford the corresponding adducts **3**. However, minor amounts of different acetonitrile adducts **6a**−**c** are also produced (Scheme 4) even when the reaction is effected in neat NCMe.

Evidently, intermediate **F** resulting from reversible hydride migration to the carbene carbon is readily accessible, being most likely stabilized by weak *O*-coordination (as other similar intermediates formulated in this paper). However, the fact that compounds **6** form in this reaction means that the trapping of **F** by acetonitrile is not fully effective, so that **F** can additionally rearrange through an alternative, competitive reaction route to give the hydride aryl compounds **6**, trapped also as acetonitrile adducts. In accord with this assumption when the heating is effected in C_6H_{12} with ca. 2 equiv of NCMe compounds **6**, the thermodynamic products are clearly predominating (eq 4), and similarly, prolonged heating of, for example, compound **3c** with 2 equiv of NCMe in cyclohexane gives **6c** in good yields (eq 5).



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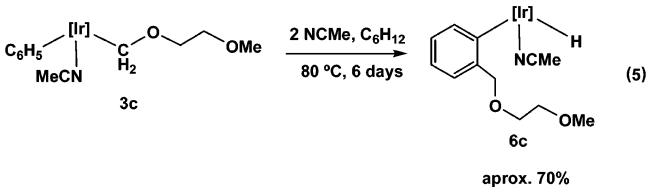
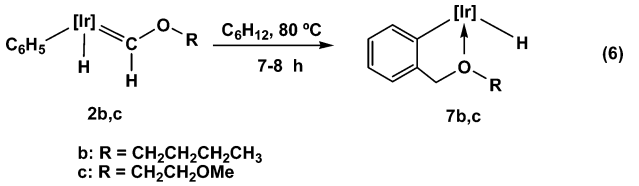


(5)

Interestingly, effecting the heating in cyclohexane in the absence of acetonitrile (eq 6) permits the isolation of the hydride aryl derivatives **7b**,**c** (the related compound **7a** derived from $MeOBu^t$ has not been observed, probably because of instability due to the steric hindrance caused by the bulky Bu^t substituent).



(6)

Compounds **6** and **7** have been characterized by microanalysis and spectroscopy, and in addition the solid-state structures of **6b** and **7b** have been determined by X-ray crystallography.

(20) (a) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. (b) Curtis, M. D.; Shiu, K. B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.

(21) Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(22) Wang, C.; Lewis, A. R.; Batchelor, R. J.; Einstein, F. W. B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1279.

(23) Chatt, J.; Johnson, N. P.; Shaw, B. L. *J. Chem. Soc.* **1964**, 1625.

(24) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (b) Millar, S. P.; Zubris, D. L.; Bercaw, J. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 5329. (c) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492.

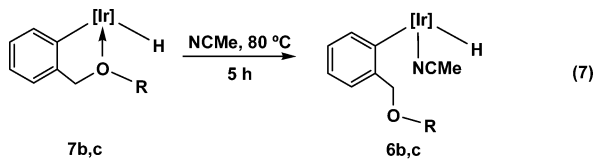
Table 1. Crystal Data and Data Collection and Refinement Details for 4b, 6b, 7b, and 8-Cl·Et_2O

	4b	6b	7b	8-Cl·Et_2O
formula	$C_{20}H_{34}BIrN_6O$	$C_{28}H_{41}BIrN_7O$	$C_{26}H_{38}BIrN_6O$	$C_{26}H_{37}BClIrN_6O_2$
mol wt	577.54	694.69	653.63	704.08
color, habit	yellow, prism	colorless, prism	yellow, needle	red, plate
symmetry, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	7.8568(5)	8.0032(3)	8.0551(4)	11.297(2)
b, Å	10.6536(6)	25.5968(11)	10.9901(5)	11.654(2)
c, Å	14.7322(9)	14.0060(6)	14.9513(7)	12.137(2)
α, deg	90.327(1)	90	82.332(1)	109.124(3)
β, deg	96.757(1)	91.226(1)	86.911(1)	99.710(3)
γ, deg	108.336(1)	90	79.531(1)	102.222(3)
V, Å^3	1161.20(12)	2868.6(2)	1289.32(11)	1425.7(4)
Z	2	4	2	2
D_{calcd}, *g* cm^{-3}	1.652	1.609	1.684	1.640
μ, mm^{-1}	5.771	4.689	5.209	4.810
θ range, deg	2.4−30.0	2.2−30.0	2.9−30.6	1.8−30.0
temp, K	173(2)	100(2)	100(2)	123(2)
no. of data collected	17 339	43 544	39 865	26 323
no. of unique data	6696 (R_{int} = 0.0193)	8357 (R_{int} = 0.0240)	7853 (R_{int} = 0.0322)	8211 (R_{int} = 0.0426)
no. of params/restraints	276/1	354/0	317/0	342/0
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0193	0.0188	0.0245	0.0243
wR2[b] (all data)	0.0472	0.0425	0.0758	0.0525

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[(w(F_o^2)^2]\}^{1/2}$.

Figures 2 and 3 show their corresponding ORTEP perspective views, demonstrating once again their somewhat distorted octahedral structures, with N−Ir−N angles close to the ideal 90° value. In the two compounds there is a σ Ir−C bond to the aryl sp^2 carbon atom. This has the expected length for a single Ir−C bond (2.00−2.05 Å), which is significantly longer than the Ir−carbene bond length of ca. 1.86 Å found for **4b**, supporting our suggestion of some Ir−C multiple character in the latter compound.

NMR monitoring of the reactions of eq 6 reveals the presence in the crude reaction products of very minor amounts of the benzyl ethers **5b**,**c**, possibly as a consequence of partial thermal decomposition and the action of adventitious water on **7**. Complexes **7** have indeed meager thermal stability, and moreover when heated in benzene, they generate the ethers **5**. These results indicate that complexes **7** are true intermediates in the route leading to **4** and **5** according to eq 3. As it can be anticipated compounds, **7b**,**c** convert readily into the acetonitrile adducts **6b**,**c** upon heating in acetonitrile (eq 7).

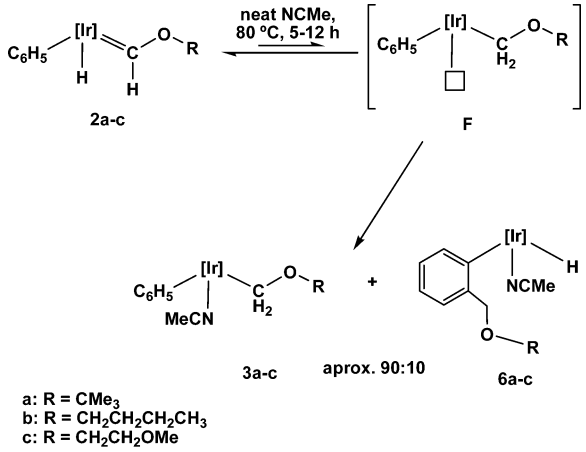


(7)

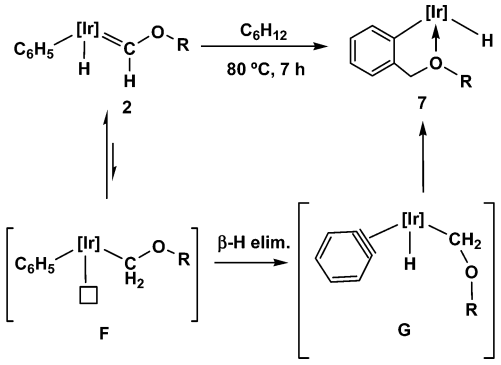
The iridium hydride complexes **6** and **7** generated from the carbenes **2** by heating in benzene in the presence of the ethers, with or without acetonitrile, contain an elaborated aryl ligand with a $-CH_2OR$ substituent (R = Bu^t, Bu^n, $CH_2OCH_2CH_2OMe$) in *ortho* position with respect to the iridium-bound carbon atom. Formation of such a group requires a C−C coupling reaction between one molecule of C_6H_6 and one of the ether, following prior cleavage of a C−H bond.

Scheme 5 shows a plausible reaction pathway involving a 1,2-H migration in **2** as the initial reaction step, to give intermediate **F** (as already indicated very likely stabilized by coordination of the oxygen atom). This process is reversible, and at 60 °C, **F** is trapped by NCMe to give the adducts **3**. Nonetheless, at sufficiently high temperatures (80−100 °C), **F** can also undergo β-H elimination to give the benzyne complex

Scheme 4



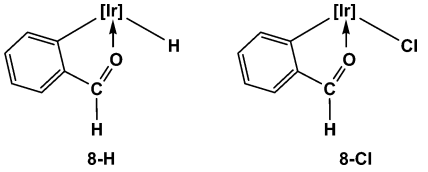
Scheme 5



intermediate **G**, which rearranges irreversibly by a C−C bond forming reaction consisting formally in the migratory insertion of the benzyne unit into the Ir−C σ bond. If acetonitrile is present, compounds **7** convert into the adducts **6**.

For the sake of completion, before ending this section by addressing the formation of the C−C coupling products **4** and **5**, it should be mentioned that compounds **8**, with the structures schematically represented below, have been generated as a result of the unexpected decomposition of **7c**.

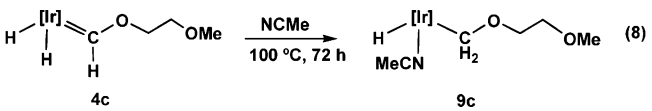
The latter compound can be isolated in microanalytically pure form by crystallization from CH_2Cl_2/hexane mixtures. However,



when subjected to column chromatography (silica gel), it converts partially into the new hydride **8-H**, in a reaction that involves formally the cleavage of the O−CH_2CH_2OMe bond of **7c**. We have paid no further attention to this decomposition process. A hydride signal at δ −22.69 is detected in the ^{1}H NMR spectrum of **8-H**, whereas the aldehyde group, −C(O)H, gives rise to ^{1}H and ^{13}C{^{1}H} resonances at 9.16 and 212.4 ppm, respectively. For the latter a value of 178 Hz can be measured for the one-bond ^{1}H−^{13}C coupling constant. Upon crystallization from CH_2Cl_2-containing mixtures of solvents, the chloride analogue **8-Cl** is obtained instead.

Figure 4 shows the molecular structure of **8-Cl**, which features an Ir−C(18) bond distance of 1.999(3) Å, which evidently corresponds to a single Ir−Csp^2 bond to the aryl functionality. This values reinforces further our proposal that the Ir−Csp^2 bond length of 1.859(2) Å found for the carbene moiety of **4b** is indicative of some multiple-bond character.

Returning to the overall conversion of compounds **2** into **4** plus **5** (eq 3), and with reference to the reaction system consisting of **1**, C_6H_6, and MeOCH_2CH_2OMe, our results and the sequence of events that explain them can be represented as depicted in Scheme 6. Briefly, heating **1** in C_6H_6 in the presence of dme yields the bis(hydride) carbene **4c** along with the ether **5c**. The reaction starts with sp^3 C−H bond activation at one of the Me termini of the diether to give **F**, followed by reversible α-H elimination to afford the hydride carbene **2c**, which in the presence of NCMe would give **3c**. As pointed out by a reviewer, conversion of **2c** into **7c** could be explained by migration of the phenyl group to the Fischer carbene, followed by *ortho* C−H activation and C,H reductive elimination. While this is a reasonable possibility, it would involve a sterically crowded, seven-coordinate Ir(V) intermediate, a situation that in our experience appears unlikely. Moreover, while the direct product of the hydride-to-carbene migration can be trapped as the corresponding NCMe adduct **3c**, the related adduct resulting from the direct phenyl-to-carbene migration has not been detected. On this basis we propose instead that the benzyne intermediate **G** could be generated and a C−C coupling lead to **7c**, which eliminates the organic product **5c** by action of a molecule of C_6H_6. Activation of a second molecule of dme by means of the sequence of events **H** → **I** → **J** in Scheme 6 gives rise to the final organometallic product of the reaction, namely, the bis(hydride) carbene compound **4c**. Unfortunately complexes **4** do not convert into **2** and dihydrogen when heated in the presence of C_6H_6, and this prevents obtaining the benzyl ethers **5** by the iridium-catalyzed coupling of C_6H_6 and the methyl ethers MeOR. The bis(hydride) carbene undergoes migratory insertion only with reluctance; the acetonitrile adduct **9c** (eq 8) requires heating at 100 °C for 3 days.



C−H Bond Activation Followed by C−O Bond Cleavage. Apart from the unexpected fragmentation of the C−O bond that leads to **8-H** as discussed previously, during the activation of MeOBu^n we have isolated compound **10b**, which contains

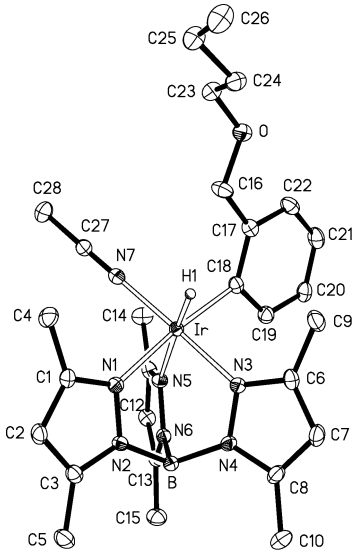


Figure 2. ORTEP view of complex **6b** (hydrogen atoms omitted for clarity except the hydride ligand). Selected bond distances (Å) and angles (deg): Ir−H(1) 1.56(3), Ir−C(18) 2.054(2), Ir−N(1) 2.143(2), Ir−N(3) 2.025(2), Ir−N(5) 2.174(2), Ir−N(7) 1.980(2), C(17)−C(18) 1.414(3), C(16)−C(17) 1.502(3), O−C(16) 1.428-(2), O−C(23) 1.427(3), N(1)−Ir−N(3) 85.4(1), N(1)−Ir−N(5) 84.5(1), N(3)−Ir−N(5) 90.3(1).

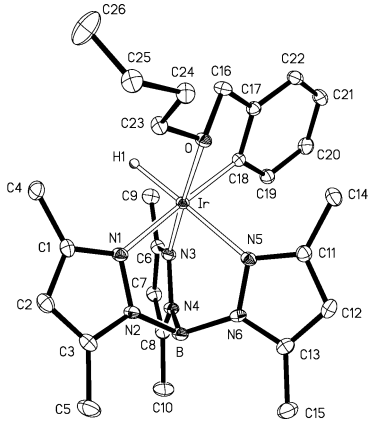
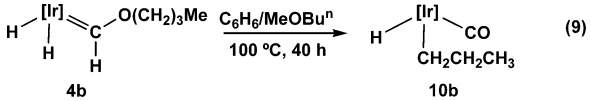


Figure 3. ORTEP representation of complex **7b** (hydrogen atoms omitted for clarity except the hydride ligand). Selected bond distances (Å) and angles (deg): Ir−H(1) 1.59, Ir−C(18) 2.004(3), Ir−N(1) 2.178(2), Ir−N(3) 2.007(2), Ir−N(5) 2.188(2), Ir−O 2.133-(2), O−C(23) 1.454(3), O−C(16) 1.471(3), N(1)−Ir−N(3) 83.0-(1), N(1)−Ir−N(5) 88.5(1), N(3)−Ir−N(5) 89.4(1).

hydride, *n*-propyl, and carbon monoxide ligands (eq 9) as a result of the selective rupture of the Me−OBu^n. Compound **10b** is detected in the reaction mixture that leads to the bis(hydride) **4b** and can be generated (30%) from the latter compound by heating in a C_6H_6/MeOBu^n mixture at 100 °C (eq 9). It features infrared absorptions at 2160 and 2000 cm^{-1}, due respectively to ν(Ir−H) and ν(Ir−CO). The latter is lower by ca. 140 wavenumbers than that for free CO (2143 cm^{-1}), indicating once again that the Ir(III) center of these compounds is electron rich enough to effect π-back-donation to good π-accepting ligands.



Mechanistic studies on eq 9 have not been carried out, as the analogous C−O cleavage of alkyl aryl ethers is being

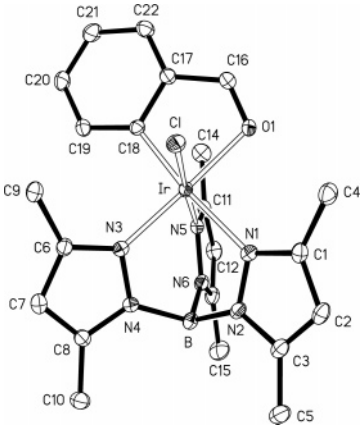
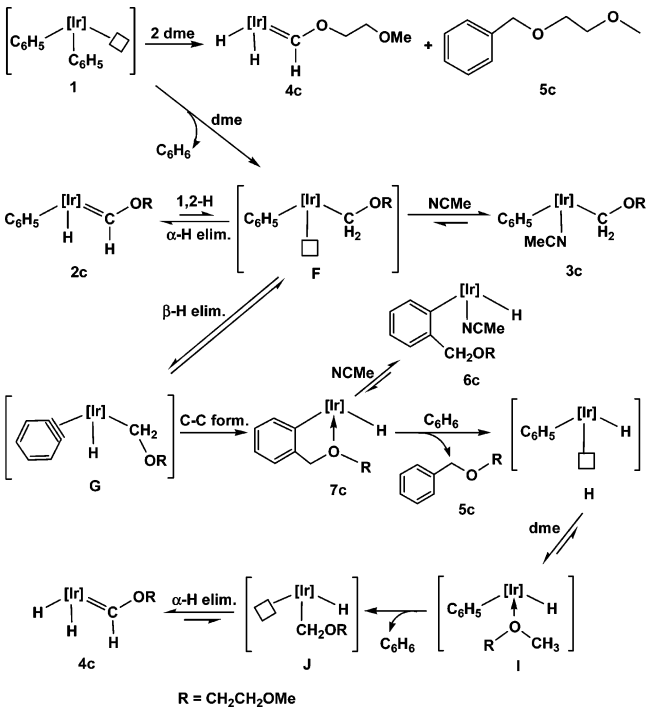
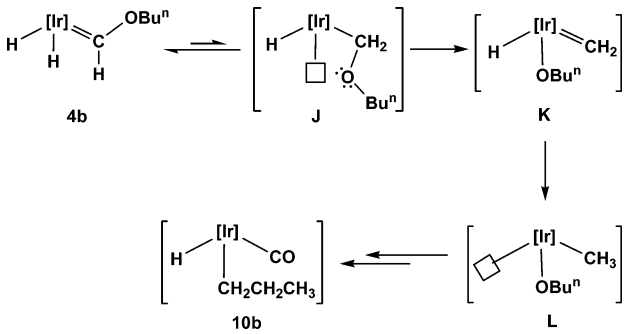


Figure 4. X-ray structure of complex **8-Cl** (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ir−Cl 2.3565(8), Ir−C(18) 1.999(3), Ir−O(1) 2.078(2), Ir−N(1) 2.154(2), Ir−N(3) 2.032(2), Ir−N(5) 2.064(2), N(1)−Ir−N(3) 88.4(1), N(1)−Ir−N(5) 86.6(1), N(3)−Ir−N(5) 88.4(1).

Scheme 6

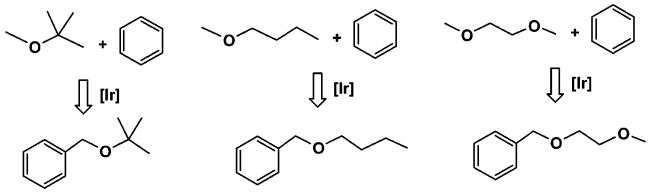


Scheme 7



investigated[11] and will be discussed in full in due course. At this stage it seems reasonable that intermediate **J** of Scheme 7 could experience an irreversible α-OBu^n elimination to give the transient methylene intermediate **K**. This would undergo a fast 1,2-H shift to give **L**, which subsequently converts into the product by well-established reaction steps (*β*-H elimination, aldehyde C−H activation with elimination of CH_4, and carbon monoxide deinsertion[25]).

Scheme 8



Conclusions

In summary, the iridium compound **1** mediates the coupling of benzene and the methyl ethers $MeOBu^t$, $MeOBu^n$, and $MeOCH_2CH_2OMe$, to give the benzyl ethers $C_6H_5CH_2OR$ shown in Scheme 8. Mechanistic studies have allowed the trapping of some key intermediates and have provided relevant information not only on the nature of the elementary steps involved in the global reaction but also with regard to the precise sequence with which they occur in the complex reaction manifold. Facile C−H activation of the ethers triggers the process, the initial step consisting in the cleavage of one of the sp^3 C−H bonds of the ether CH_3O- group, followed by a reversible α-H elimination. This C−H bond cleavage is assisted by coordination of the ether oxygen atom, and it is followed by an aromatic C−H bond activation of a coordinated phenyl group (*β*-H elimination) to give a putative benzyne intermediate that participates in the C−C coupling reaction. Following the steps represented in Scheme 6, complexes **4** and the organic products **5** become the end products of this rearrangement. Failure of the bis(hydride) carbene compounds **4** to regenerate the hydride−phenyl−carbene derivatives **2** has so far prevented us effecting this transformation under catalytic conditions. In addition to the above elemental reactions cleavage of the Me−OBu^n has also been demonstrated when compound **1** is reacted with methyl *n*-butyl ether. This reaction is somewhat more energetically demanding than the C−H bond activation and the C−C coupling, but it is actually competitive and compound **10b** is always detected in the reactions leading to **4b** and **5b**.

Experimental Section

General Procedures. Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained with a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(C_2H_4)_2$[26] and $Tp^{Me2}Ir(C_6H_5)_2(N_2)$[12] were obtained by published procedures.

$Tp^{Me2}Ir(Ph)(H)(=C(H)OBu^t)$ (2a). Compound $Tp^{Me2}Ir(C_2H_4)_2$ (0.40 g, 0.733 mmol) was dissolved in C_6H_6 (15 mL), $CH_3OC(CH_3)_3$ (0.434 mL, 3.67 mmol) was added, and the solution was

(25) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248.

(26) Alvarado, Y.; Bountry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem.−Eur. J.* **1997**, *3*, 860.

stirred for 30 min at 80 °C. Then the solvent was removed under reduced pressure, and the solid residue was chromatographed on silica gel (40:1 → 10:1 hexane/Et_2O) to obtain compound **2a** in 65% yield. ^{1}H NMR ($CDCl_3$): δ 15.65 (s, 1 H, Ir=CH), 8.09, 7.05, 6.84, 6.70, 6.40 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7$ Hz, 5 CH_{ar}), 5.87, 5.81, 5.71 (s, 1 H each, 3 CH_{pz}), 2.55, 2.45, 2.44, 2.14, 1.62, 1.60 (s, 3 H each, 6 Me_{pz}), 1.51 (s, 9 H, CMe_3), −17.29 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 252.9 ($^1J_{CH} = 146$ Hz, Ir=CH), 152.1, 149.9, 149.0, 143.6, 143.3, 143.2 (C_{qpz}), 141.7, 139.6, 125.8, 120.4 (1:1:2:1, CH_{ar}), 136.4 (C_{qar}), 106.1, 106.1, 105.3 (CH_{pz}), 89.0 (CMe_3), 28.6 (CMe_3), 15.7, 14.8, 14.1, 12.8, 12.7 (1:1:1:2:1, Me_{pz}). IR (nujol): ν(Ir−H) = 2140 cm^{-1}. Anal. Calcd for $C_{26}H_{38}BN_6OIr$: C, 47.8; H, 5.8; N, 12.9. Found: C, 47.8; H, 5.7; N, 13.2.

$Tp^{Me2}Ir(Ph)(H)(=C(H)OBu^n)$ (2b). This compound was obtained in 50% yield by following a procedure similar to that described for complex **2a**. ^{1}H NMR ($CDCl_3$): δ 15.23 (br s, 1 H, Ir=CH), 8.05, 7.05, 6.84, 6.70, 6.39 (br s, br s, t, br s, br s, 1 H each, $^3J_{HH} \approx 7$ Hz, 5 CH_{ar}), 5.84, 5.79, 5.70 (s, 1 H each, 3 CH_{pz}), 4.37, 4.30 (br s, 1 H each, OCH_2), 2.51, 2.42, 2.41, 2.07, 1.65, 1.54 (s, 3 H each, 6 Me_{pz}), 1.78 (br s, 2 H, OCH_2CH_2), 1.39 (br s, 2 H, CH_2CH_3), 0.93 (br s, 3 H, CH_2CH_3), −16.53 (br s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 261.0 (br s, $^1J_{CH} = 144$ Hz, Ir=CH), 152.3, 149.5, 148.7, 143.6, 143.4, 143.2 (C_{qpz}), 141.7, 139.6, 126.0, 120.6 (br s, br s, s, s, 1:1:2:1, CH_{ar}), 136.0 (C_{qar}), 106.2, 106.1, 105.3 (CH_{pz}), 84.0 (br s, $^1J_{CH} = 144$ Hz, OCH_2), 31.8 (br s,$^1J_{CH} =$ 128 Hz, OCH_2CH_2), 18.8 ($^1J_{CH} = 126$ Hz, CH_2CH_3), 15.5, 14.8, 13.6, 12.7, 12.7 (1:1:1:2:1, Me_{pz}), 14.0 (br s, CH_2CH_3). IR (nujol): ν(Ir−H) 2139 cm^{-1}. Anal. Calcd for $C_{26}H_{38}BN_6OIr$: C, 47.8; H, 5.8; N, 12.9. Found: C, 48.2; H, 5.7; N, 13.0.

$Tp^{Me2}Ir(Ph)(H)(=C(H)OCH_2CH_2OCH_3)$ (2c). By the same general method, but heating the solution at 60 °C for 6 h and using a 7:1 hexane/Et_2O mixture as eluent, complex **2c** was obtained in ca. 85% yield. ^{1}H NMR ($CDCl_3$): δ 15.17 (br s, 1 H, Ir=CH), 8.01, 7.02, 6.81, 6.67, 6.34 (br s, br s, t, br s, br s, 1 H each, $^3J_{HH} \approx 7$ Hz, 5 CH_{ar}), 5.81, 5.76, 5.67 (s, 1 H each, 3 CH_{pz}), 4.46 (br m, 2 H, $OCH_2CH_2OCH_3$), 3.60 (m, 2 H, $OCH_2CH_2OCH_3$), 3.29 (s, 3 H, OCH_3), 2.48, 2.39, 2.37, 1.63, 1.51 (s, 3 H each, 5 Me_{pz}), 2.05 (br s, Me_{pz}), −16.46 (br s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 262.9 (br s, $^1J_{CH} = 169$ Hz, Ir=CH), 152.3, 149.7, 143.4 (1:2:3, C_{qpz}), 141.5, 139.5, 126.0, 120.6 (br s, br s, s, s, 1:1:2:1, *o*, *m*, and *p*-CH_{ar} respectively), 135.8 (br s, C_{qar}), 106.2, 106.1, 105.3 (CH_{pz}), 82.4 (br s, $^1J_{CH} = 144$ Hz, $OCH_2CH_2OCH_3$), 70.3 ($^1J_{CH} = 141$ Hz, $OCH_2CH_2OCH_3$), 58.8 ($^1J_{CH} = 139$ Hz, OCH_3), 15.3, 14.7, 13.8, 12.7, 12.6 (1:1:1:2:1, Me_{pz}). IR (nujol): ν(Ir−H) 2140 cm^{-1}. Anal. Calcd for $C_{25}H_{36}BN_6O_2Ir$: C, 45.8; H, 5.5; N, 12.8. Found: C, 45.8; H, 5.5; N, 12.8.

$Tp^{Me2}Ir(Ph)(CH_2OBu^t)(NCMe)$ (3a). Compound **2a** (0.050 g, 0.77 mmol) was dissolved in NCMe, and the solution was stirred for 12 h at 80 °C. Then the solvent was removed under reduced pressure, and the solid residue was dissolved in CH_2Cl_2. An excess of pentane was added, and compound **3a** precipitated as a white solid (55% yield). ^{1}H NMR ($CDCl_3$): δ 7.78, 7.05, 6.82, 6.64, 6.45 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7$ Hz, *o*, *m*, *p*, *m*′, *o*′-CH_{ar}), 5.82, 5.68, 5.58 (s, 1 H each, 3 CH_{pz}), 4.79, 4.53 (d, d, 1 H each, $^2J_{HH} = 4.9$ Hz, Ir−CH_2O), 2.59, 2.44, 2.39, 2.38, 2.37, 1.49, 1.48 (s, 3 H each, 6 Me_{pz} + NCMe), 1.21 (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.6, 150.9, 149.6, 143.3, 143.0, 142.4 (C_{qpz}), 140.3, 137.8, 125.5, 125.1, 120.1 (CH_{ar}), 111.3 (NCMe), 108.0, 106.6, 106.3 (CH_{pz}), 71.4 (CMe_3), 31.4 ($^1J_{CH} = 138$ Hz, Ir−CH_2O), 27.9 ($^1J_{CH} = 138$ Hz, CMe_3) 13.8, 13.4, 13.3, 13.1, 12.6, 12.5, 3.7 (Me_{pz} + NC*Me*). IR (nujol): ν(CN) = 2284 cm^{-1}.

$Tp^{Me2}Ir(Ph)(CH_2OBu^n)(NCMe)$ (3b). This complex was obtained similarly to **3a** (50% yield). ^{1}H NMR ($CDCl_3$): δ 7.39, 7.06, 6.82, 6.66, 6.48 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7$ Hz, *o*, *m*, *p*, *m*′, *o*′-CH_{ar}), 5.80, 5.68, 5.56 (s, 1 H each, 3 CH_{pz}), 4.98, 4.73 (d, d, 1 H each, $^2J_{HH} = 6.1$ Hz, Ir−CH_2O), 3.33 (m, 2 H, OCH_2), 2.46, 2.39, 2.38, 2.35, 1.49, 1.46 (1:2:1:1:1:1, 6 Me_{pz} + NCMe), 1.53 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 1.32 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 0.88 (t, 3 H, $^3J_{HH} = 7.3$ Hz, $OCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.0, 150.8, 149.5, 143.0, 142.8, 142.4 (C_{qpz}), 140.3, 137.0, 126.0, 125.3, 120.3 (*o*′, *o*, *m*′, *m*, *p*-CH_{ar}), 138.4 (C_{qar}), 112.0 (NCMe), 107.7, 106.6, 106.3 (CH_{pz}), 72.7 ($^1J_{CH} = 136$ Hz, OCH_2-$CH_2CH_2CH_3$), 46.0 ($^1J_{CH} = 138$ Hz, Ir−CH_2O), 32.4 ($^1J_{CH} = 121$, $OCH_2CH_2CH_2CH_3$), 19.8 ($^1J_{CH} = 126$ Hz, $OCH_2CH_2CH_2CH_3$), 14.1, 13.7, 13.4, 13.3, 12.7, 12.5, 12.4 (Me_{pz} + $OCH_2CH_2CH_2CH_3$), 3.8 (NC*Me*). IR (nujol): ν(CN) = 2287.4 cm^{-1}.

$Tp^{Me2}Ir(Ph)(CH_2OCH_2CH_2OCH_3)(NCMe)$ (3c). A solution of **2c** (0.053 g, 0.08 mmol) in NCMe (4 mL) was stirred at 80 °C for 5 h, after which time the solvent was distilled off under reduced pressure. Crystallization from hexane/CH_2Cl_2 (2:1) at −20 °C gave the product **3c** as thin, white needles (0.045 g, isolated yield 80%). ^{1}H NMR ($CDCl_3$): δ 7.30, 7.05, 6.82, 6.66, 6.46 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7$ Hz, *o*, *m*, *p*, *m*′, *o*′-CH_{ar}), 5.79, 5.68, 5.58 (s, 1 H each, 3 CH_{pz}), 5.09, 4.82 (d, d, 1 H each, $^2J_{HH} = 6.3$ Hz, Ir−CH_2O), 3.47 (m, 4 H, OCH_2CH_2O), 3.27 (s, 3 H, OCH_3), 2.45, 2.42, 2.38, 2.37, 2.35, 1.49, 1.44 (s, 3 H each, 6 Me_{pz} + $NCCH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.0, 150.9, 149.6, 143.1, 142.8, 142.4 (C_{qpz}), 140.3, 136.8, 126.0, 125.5, 120.4 (*o*′, *o*, *m*′ *m*, *p*-CH_{ar}), 138.2 (C_{qar}), 112.4 (NCMe), 107.8, 106.6, 106.4 (CH_{pz}), 72.2, 71.8 ($^1J_{CH}$ = 136 y 139 Hz, OCH_2CH_2O), 58.7 ($^1J_{CH} = 140$ Hz, OCH_3), 47.1 ($^1J_{CH} = 138$ Hz, Ir−CH_2O), 13.7, 13.4, 13.4, 12.7, 12.5 (1:1:1:2:1, Me_{pz}), 3.8 (s, 3 H, NCMe). IR (nujol): ν(CN) 2284 cm^{-1}. Anal. Calcd for $C_{27}H_{39}BN_7O_2Ir$: C, 46.6; H, 5.6; N, 14.1. Found: C, 46.6; H, 5.7; N, 14.0.

$Tp^{Me2}Ir(H)_2(=C(H)OBu^t)$ (4a) and $C_6H_5CH_2OBu^t$ (5a). Compound $Tp^{Me2}Ir(C_2H_4)_2$ (0.300 g, 0.549 mmol) was dissolved in C_6H_6 (10 mL), and CH_3OCMe_3 (0.651 mL, 5.49 mmol) was added. The solution was stirred for 16 h at 100 °C, and after this period of time, the solvent was removed under reduced pressure. NMR spectra of the crude product revealed the presence of compound **4a** and the organic derivative **5a**. Following column chromatography on silica gel (hexane → hexane/Et_2O), compound **4a** (15% yield) and the organic product **5a** (20% yield) were isolated. **4a**: ^{1}H NMR ($CDCl_3$): δ 15.70 (s, 1 H, Ir=CH), 5.78, 5.72 (s, 2:1, 3 CH_{pz}), 2.41, 2.33, 2.32, 2.04 (s, 2:1:1:2, 6 Me_{pz}), 1.42 (s, 9 H, CMe_3), −17.74 (s, 2 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 246.9 (br s, $^1J_{CH}$ =146 Hz, Ir=CH), 151.78, 149.7, 143.7, 143.6 (1:2:1:2, C_{qpz}), 105.3 (CH_{pz}), 87.5 (CMe_3), 28.4 ($^1J_{CH} = 126$ Hz, CMe_3) 17.3, 15.6, 12.7, 12.5 (1:2:2:1, Me_{pz}). IR (nujol): ν(Ir−H) = 2136.5 cm^{-1}. **5a**: ^{1}H NMR ($CDCl_3$): δ 7.33 (m, 5 H, CH_{ar}), 4.44 (s, 2 H, $PhCH_2O$), 1.29 (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.3 (C_{qar}), 127.7, 126.8, 126.5 (2:2:1, CH_{ar}), 72.8 (CMe_3), 63.6 ($PhCH_2O$), 27.1 (CMe_3). SM *m*/*z*: 164 (M^+).

$Tp^{Me2}Ir(H)_2(=C(H)OBu^n)$ (4b) and $C_6H_5CH_2OBu^n$ (5b). These compounds were obtained by following a procedure similar (100 °C, 5 h) to that described for **4a** and **5a**. The chromatographic yields were 40% and 60% for **4b** and **5b**, respectively. Compound **4b** could be crystallized from a ethanol/Et_2O mixture. **4b**: ^{1}H NMR ($CDCl_3$): δ 15.28 (s, 1 H, Ir=CH), 5.77, 5.74 (s, 2:1, 3 CH_{pz}), 4.62 (br s, 2 H, OCH_2), 2.40, 2.35, 1.91 (s, 1:1:1, 6 Me_{pz}), 1.91 (m, 2 H, OCH_2CH_2), 1.52 (m, 2 H, CH_2CH_3), 1.00 (t, 3 H, $^3J_{HH} =$ 7.1 Hz, CH_2CH_3), −17.97 (br s, 2 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 261.5 (br s, Ir=CH), 152.4, 149.8, 144.5, 143.7 (1:2: 1:2, C_{qpz}), 105.6, 105.4 (2:1, CH_{pz}), 81.8 (br s, $^1J_{CH} = 149$ Hz, OCH_2), 30.6 (br s, $^1J_{CH} = 126$ Hz, OCH_2CH_2), 19.6 (br s, $^1J_{CH} =$ 124 Hz, CH_2CH_3), 17.3, 15.6, 12.9 (1:2:3, Me_{pz}), 14.1 (CH_2CH_3). IR (nujol): ν(Ir−H) = 2148 cm^{-1}. Anal. Calcd for $C_{20}H_{34}BN_6OIr$: C, 41.7; H, 5.9; N, 14.6. Found: C, 41.7; H, 5.6; N, 14.2. **5b**: ^{1}H NMR ($CDCl_3$): δ 7.29 (m, 5 H, 5 CH_{ar}), 4.49 (s, 2 H, $PhCH_2O$), 3.46 (t, $^3J_{HH} = 6.5$ Hz, 2 H, $OCH_2CH_2CH_2CH_3$), 1.59 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 1.38, (m, 2 H, $CH_2CH_2CH_3$), 0.90 (t, $^3J_{HH} =$ 7.3 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 139.0 (C_{qar}), 128.6, 127.9, 127.7 (2:2:1, CH_{ar}), 78.7 ($PhCH_2O$), 77.3

($OCH_2CH_2CH_2CH_3$), 32.1 ($OCH_2CH_2CH_2CH_3$), 19.7 ($OCH_2CH_2CH_2CH_3$), 14.2 (CH_2CH_3).

$Tp^{Me2}Ir(H)_2(=C(H)OCH_2CH_2OCH_3)$ (4c) and $C_6H_5CH_2OCH_2CH_2OCH_3$ (5c). By the same general method, but heating at 80 °C for 24 h, compounds **4c** and **5c** were obtained. The chromatographic yields were 30% and 60% for **4c** and **5c**, respectively. Compound **4c** could be crystallized from a hexane/CH_2Cl_2 mixture (3:2) by cooling to −20 °C. **4c**: ^{1}H NMR ($CDCl_3$): δ 15.39 (s, 1 H, Ir=CH), 5.81, 5.79 (s, 2:1, 3 CH_{pz}), 4.84 (br s, 2 H, $OCH_2CH_2OCH_3$), 3.94 (br s, 2 H, $OCH_2CH_2OCH_3$), 3.48 (br s, 3 H, OCH_3), 2.44, 2.39, 2.39, 1.95 (s, 2:1:1:2, 6 Me_{pz}), −17.80 (br s, 2 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 262.3 (br s, $^1J_{CH}$ = 150 Hz, Ir=CH), 152.2, 149.6, 144.2, 143.6 (1:2:1:2, C_{qpz}), 105.5 (CH_{pz}), 80.3 (br s, $^1J_{CH}$ = 146 Hz, $OCH_2CH_2OCH_3$), 70.2 ($^1J_{CH}$ = 145 Hz, $OCH_2CH_2OCH_3$), 59.1 ($^1J_{CH}$ = 141 Hz, OCH_3), 17.2, 15.4, 12.7 (1:2:3, Me_{pz}). IR (nujol): ν(Ir−H) 2135 cm^{-1}. Anal. Calcd for $C_{19}H_{32}BN_6O_2Ir$: C, 39.4; H, 5.6; N, 14.5. Found: C, 39.5; H, 5.5; N, 14.2. **5c**: ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 5 H, 5 CH_{ar}), 4.57 (s, 2 H, $PhCH_2O$), 3.60 (m, 4 H, $OCH_2CH_2OCH_3$), 3.38 (s, 3 H, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.2 (C_{qar}), 128.4, 127.8, 127.7 (2:2:1, CH_{ar}), 73.4 ($PhCH_2O$), 72.0, 69.3 ($OCH_2CH_2OCH_3$), 59.1 (OCH_3). MS *m*/*z*: 166.0 (M^+), 107.0 (M^+ − 59), 92.0 (M^+ − 74), 77.0 (M^+ − 89).

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$CH_2OBu^t)(NCMe)$ (6a). Compound **2a** (0.50 g, 0.77 mmol) was dissolved in C_6H_{12}, and NCMe (8 μL, 1.54 mmol) was added. The solution was stirred for 48 h at 80 °C, and after that period of time, a white precipitate of **6a** was filtered off and washed with pentane (2 × 2 mL) (65% yield). ^{1}H NMR ($CDCl_3$): δ 7.28, 6.82, 6.49, 6.45 (d, t, t, d, 1 H each, $^3J_{HH} \approx 7$ Hz, 4 CH_{ar}), 5.79, 5.78, 5.54 (s, 1 H each, 3 CH_{pz}), 4.99, 4.98 (d, d, 1 H each, $^2J_{HH}$ =11.9 Hz, $ArCH_2O$), 2.44, 2.37, 2.34, 1.69, 1.29 (1:3:1:1:1, 6 Me_{pz} + $NCCH_3$), 1.39 (s, 9 H, CMe_3), −20.37 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.7, 150.0, 149.6, 143.3, 142.9, 142.8 (C_{qpz}), 146.1, 134.7 (C_{qar}), 140.9, 124.1, 124.0, 120.9 (CH_{ar}), 114.9 (NCMe), 106.3, 105.9, 105.4 (CH_{pz}), 72.5 (CMe_3), 69.2 ($^1J_{CH}$ = 139 Hz, $ArCH_2O$), 28.2 (CMe_3), 15.1, 14.5, 13.8, 13.0, 12.5, 12.4 (Me_{pz}), 4.0 (NC*Me*). IR (nujol): ν(CN) 2284, ν(Ir−H) 2158 cm^{-1}. Anal. Calcd for $C_{28}H_{41}BN_7OIr$: C, 48.4; H, 5.9; N, 14.1. Found: C, 47.7, H, 5.2; N, 13.8.

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$CH_2OBu^n)(NCMe)$ (6b). This compound was obtained by following the method described for **6a** (80 °C, 24 h; 90% yield). It could be crystallized from a CH_2Cl_2/Et_2O (1:2) mixture at −20 °C. ^{1}H NMR ($CDCl_3$): δ 7.22, 6.82, 6.51, 6.43 (d, t, t, d, 1 H each, $^3J_{HH} \approx 7.5$ Hz, 4 CH_{ar}), 5.79, 5.76, 5.55 (s, 1 H each, 3 CH_{pz}), 5.15, 5.02 (d, d, 1 H each, $^2J_{HH}$ =12.1 Hz, $ArCH_2O$), 3.61 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 2.43, 2.36, 2.35, 2.33, 1.64, 1.41, 1.30 (6 Me_{pz} + NCMe), 1.70 (m, 2 H, $OCH_2CH_2CH_2CH_3$) 1.46 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 0.94 (t, 3 H, $^3J_{HH}$ = 136 Hz, $OCH_2CH_2CH_2CH_3$), −20.33 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 151.6, 150.1, 149.6, 143.4, 143.0, 142.8 (C_{qpz}), 145.1, 136.2 (C_{qar}), 141.3, 124.4, 124.3, 120.8 (CH_{ar}), 114.8 (NCMe), 106.3, 105.9, 105.5 (CH_{pz}), 78.0 ($^1J_{CH}$ = 141 Hz, $ArCH_2O$), 69.9 ($^1J_{CH}$ = 139 Hz, $OCH_2CH_2CH_2CH_3$), 32.4 ($^1J_{CH}$ = 123 Hz, $OCH_2CH_2CH_2CH_3$), 19.6 ($^1J_{CH}$ = 125 Hz, $OCH_2CH_2CH_2CH_3$), 15.3, 14.7, 14.2, 13.7, 12.5 (2:1:1:1:2, Me_{pz} + $OCH_2CH_2CH_2CH_3$), 3.8 (NC*Me*). IR (nujol): ν(CN) = 2283, ν(Ir−H) = 2144.3 cm^{-1}. Anal. Calcd for $C_{28}H_{41}BN_7OIr$: C, 48.4; H, 5.9; N, 14.1. Found: C, 48.0, H, 5.6; N, 14.0.

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$CH_2OCH_2CH_2OCH_3)(NCMe)$ (6c). According to the already described general method (80 °C, 24 h), this complex was obtained in 70% yield as a white solid. It was crystallized from pentane/CH_2Cl_2 mixtures (2:1) at −20 °C. Compound **6c** could be prepared alternatively by heating compound **3c** in C_6H_{12} in the presence of NCMe (1−2 equiv, 80 °C, 6 days). ^{1}H NMR ($CDCl_3$): δ 7.23, 6.82, 6.49, 6.43 (d, t, t, d, 1 H each, $^3J_{HH} \approx 7.5$ Hz, 4 CH_{ar}), 5.79, 5.78, 5.56 (s, 1 H each, 3 CH_{pz}), 5.19 (s, 2 H, $ArCH_2O$), 3.75, 3.66 (m, 2 H each, OCH_2CH_2O), 3.41 (s, 3 H, OCH_3), 2.44, 2.37, 2.34, 1.64, 1.30 (s, 1:3:1:1:1, 6 Me_{pz} + NCMe), −20.31 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.5, 150.1, 149.7, 143.4, 143.0, 142.8 (C_{qpz}), 144.6, 136.9 (C_{qar}), 141.5, 124.6, 124.5, 120.7 (CH_{ar}), 115.1 (NCMe), 106.3, 105.9, 105.5 (CH_{pz}), 78.5 ($^1J_{CH}$ = 142 Hz, $ArCH_2O$), 72.4, 68.8 ($^1J_{CH}$ = 144 Hz, OCH_2CH_2O), 59.0 ($^1J_{CH}$ = 141 Hz, OCH_3), 15.2, 14.7, 13.7, 13.1, 12.5 (1:1:1:1:2:1, Me_{pz}), 3.8 (NC*Me*). IR (nujol): ν(CN) 2282, ν(Ir−H) 2137 cm^{-1}. Anal. Calcd for $C_{27}H_{39}BN_7O_2Ir\cdot 0.5\ CH_2Cl_2$: C, 44.7; H, 5.4; N, 13.3. Found: C, 44.3; H, 5.0; N, 13.4.

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$CH_2OBu^n)$ (7b). Compound **2b** (0.10 g, 0.153 mmol) was dissolved in C_6H_{12} (10 mL), and the solution was stirred for 8 h at 80 °C. After this time, the solvent was removed under reduced pressure and the solid residue washed with pentane (2 × 2 mL), yielding **7b** as a light brown solid (84% yield). It could be crystallized by the slow evaporation of its solution in a CH_2Cl_2/pentane (2:5) mixture at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.00, 6.86, 6.81 (d, m, m, 1:1:2, $^3J_{HH}$ = 5.5 Hz, 4 CH_{ar}), 5.87, 5.69, 5.65 (s, 1 H each, 3 CH_{pz}), 5.24, 5.04 (d, d, 1 H each, $^2J_{HH}$ = 10.1 Hz, $ArCH_2O$), 3.84, 3.66 (m, m, 1 H each, OCH_2CH_2), 2.48, 2.44, 2.42, 2.36, 2.02, 1.30 (s, 3 H each, 6 Me_{pz}), 1.43 (m, $CH_2CH_2CH_3$), 1.10 (m, $CH_2CH_2CH_3$), 0.76 (t, $^3J_{HH}$ = 7.8 Hz, $CH_2CH_2CH_3$), −21.57 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.7, 151.2, 150.2, 143.9, 143.0, 142.7 (C_{qpz}), 145.3, 144.0 (C_{qar}), 136.8, 124.7, 119.5, 118. 2 (CH_{ar}), 106.8, 105.8, 105.4 (CH_{pz}), 87.7 ($^1J_{CH}$ = 144 Hz, $ArCH_2O$), 79.7 ($^1J_{CH}$ = 146 Hz, OCH_2), 30.1 ($^1J_{CH}$ = 130 Hz, OCH_2CH_2), 18.36 ($^1J_{CH}$ = 126 Hz, CH_2CH_3), 16.4, 15.9, 13.1, 12.6, 12.6, 12.0 (Me_{pz}), 13.8 (CH_2CH_3). IR (nujol): ν(Ir−H) = 2145 cm^{-1}. Anal. Calcd for $C_{26}H_{38}BN_6OIr$: C, 47.8; H, 5.8; N, 12.9. Found: C, 47.3; H, 5.5; N, 12.7.

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$CH_2OCH_2CH_2OCH_3)$ (7c). Compound **2c** (0.040 g, 0.061 mmol) was dissolved in C_6H_{12} (3 mL), and the solution was stirred for 7 h at 80 °C. The brown solution (>70% spectroscopic, ^{1}H NMR, yield of **7c**) thus obtained was dried under reduced pressure, the residue was dissolved in Et_2O (2 mL), and pentane (4 mL) was added to precipitate **7c** as a brown solid (0.012 g, 30% yield). A sample of analytical purity could be obtained by cooling to −20 °C a solution of **7c** in a hexane/CH_2Cl_2 (2:1) mixture. ^{1}H NMR ($CDCl_3$): δ 7.00, 6.86, 6.80 (m, m, m, 1:1:2, 4 CH_{ar}), 5.85, 5.67, 5.63 (s, 1 H each, 3 CH_{pz}), 5.39, 5.15 (d, 1 H each, $^2J_{HH}$ = 10.2 Hz, $ArCH_2O$), 3.97, 3.80 (ddd, 1 H each, $^2J_{HH}$ = 12.4, $^3J_{HH}$ = 5.0, 3.1 and 6.7, 3.1 Hz, respectively, $OCH_2CH_2OCH_3$), 3.18 (m, 2 H, $OCH_2CH_2OCH_3$), 3.11 (s, 3 H, OCH_3), 2.47, 2.41, 2.40, 2.33, 2.00, 1.30 (s, 3 H each, 6 Me_{pz}), −21.54 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.7, 151.4, 150.1, 143.8, 143.1, 142.7 (C_{qpz}), 145.5, 143.9 (C_{qar}), 136.8, 124.7, 119.6, 118.4 (CH_{ar}), 106.8, 105.8, 105.5 (CH_{pz}), 90.0 ($^1J_{CH}$ = 146 Hz, $ArCH_2O$), 78.0 ($^1J_{CH}$ = 145 Hz, $OCH_2CH_2OCH_3$), 71.6 ($^1J_{CH}$ = 142 Hz, $OCH_2CH_2OCH_3$), 58.7 ($^1J_{CH}$ = 141 Hz, OCH_3), 16.4, 15.8, 13.1, 12.6, 12.6, 11.8 (Me_{pz}). IR (nujol): ν(Ir−H) 2123 cm^{-1}. Anal. Calcd for $C_{25}H_{36}BN_6O_2Ir$: C, 45.8; H, 5.5; N, 12.8. Found: C, 45.5; H, 5.4; N, 12.3.

$Tp^{Me2}Ir(H)(C_6H_4$-*o*-$C(O)H)$ (8-H). Compound **2c** (0.172 g, 0.263 mmol) was dissolved in C_6H_{12} (15 mL), and the solution was stirred for 7 h at 80 °C. After this time, the solvent was removed under reduced pressure and the solid residue was chromatographed on silica gel (hexane/Et_2O, 20:1) to yield **8-H** in 20% isolated yield (0.031 g). In an attempt to crystallize it from a hexane/Et_2O/CH_2Cl_2 mixture, at −20 °C, crystals of **8-Cl** were obtained (this complex has been characterized only by X-ray diffraction analysis). ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.16 (s, 1 H, C(O)H), 7.80, 7.60, 7.01, 6.95 (dd, d, td, td, 1 H each, $^3J_{HH} \approx 7.5$, $^4J_{HH} \approx 1.4$ Hz, 4 CH_{ar}), 5.88, 5.81, 5.50 (s, 1 H each, 3 CH_{pz}), 2.43, 2.38, 2.38, 2.33, 2.14, 1.02 (s, 3 H each, 6 Me_{pz}), −22.69 (br s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 212.4 ($^1J_{CH}$ = 178 Hz, C(O)H), 175.5 (C_{qar}), 152.2, 151.8, 151.5, 148.6, 143.9, 143.4, 142.8 (C_{qpz} + C_{qar}), 138.1, 133.8, 132.5, 119.7 (CH_{ar}), 106.7, 106.4, 105.9 (CH_{pz}), 16.4, 14.4,

13.1, 12.4, 12.4, 11.7 (Me_{pz}). Anal. Calcd for $C_{22}H_{27}BN_6ClOIr\cdot 0.25Et_2O$: C, 42.6; H, 4.5; N, 12.9. Found: C, 42.4; H, 4.5; N, 12.5.

$Tp^{Me2}Ir(H)(CH_2OCH_2CH_2OCH_3)(NCMe)$ (9c). A solution of **4c** (0.096 g, 0.17 mmol) in NCMe (5 mL) was stirred at 100 °C for 3 days, after which time the solvent was distilled off under reduced pressure. At this stage, ^{1}H NMR monitoring demonstrated quantitative formation of the acetonitrile adduct **9c**, which was isolated as a pure, white crystalline solid, by crystallization from hexane/dichloromethane (2:1) at −20 °C (0.063 g, yield 60%). ^{1}H NMR ($CDCl_3$): 5.79, 5.72, 5.68 (s, 1 H each, 3 CH_{pz}), 5.12, 4.96 (d, d, 1 H each, $^2J_{HH}$ = 7.4 Hz, Ir−CH_2O), 3.72, 3.58 (m, 2 H each, OCH_2CH_2O), 3.35 (s, 3 H, OCH_3), 2.42, 2.38, 2.37, 2.35, 2.30, 2.29, 2.24 (s, 3 H each, 6 Me_{pz} + NCMe), −21.08 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.5, 150.0, 149.5, 143.2, 143.1, 142.9 (C_{qpz}), 113.7 (N*C*Me), 106.6, 106.2, 105.2 (CH_{pz}), 72.5, 71.4 ($^1J_{CH}$ = 143 and 140 Hz, OCH_2CH_2), 58.7 ($^1J_{CH}$ = 140 Hz, OCH_3), 42.9 ($^1J_{CH}$ = 137 Hz, Ir−CH_2O), 15.2, 14.5, 13.1, 13.0, 12.5, 12.4 (Me_{pz}), 3.9 (NC*Me*). IR (nujol): ν(CN) 2284, ν(Ir−H) 2153 cm^{-1}. Anal. Calcd for $C_{21}H_{35}BN_7O_2Ir$: C, 40.6; H, 5.7; N, 15.8. Found: C, 40.7; H, 5.6; N, 15.6.

$Tp^{Me2}Ir(H)(CH_2CH_2CH_3)(CO)$ (10b). Compound $Tp^{Me2}Ir(C_2H_4)_2$ (0.250 g, 0.458 mmol) was dissolved in C_6H_6 (10 mL), and $CH_3OCH_2CH_2CH_2CH_3$ (0.543 mL, 4.58 mmol) was added. The solution was stirred for 40 h at 100 °C, and after this period of time, the solvent was removed under reduced pressure. Following column chromatography on silica gel (hexane → hexane/Et_2O (200:1)) compound **10b** was isolated (15% yield). ^{1}H NMR ($CDCl_3$): 5.84, 5.81, 5.72 (s, 1 H each, 3 CH_{pz}), 2.40, 2.38, 2.34, 2.33, 2.30, 2.19 (s, 3 H each, 6 Me_{pz}), 2.02, 1.37 (td, 1 H each, $^2J_{HH} \approx$ 11.0, $^3J_{HH}$ = 6.0 Hz, Ir−CH_2), 1.67 (m, 2 H, CH_2CH_3), 0.92 (t, 3 H, $^2J_{HH}$ = 7.1 Hz, CH_2CH_3), −17.16 (br s, 2 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.0 (CO), 151.1, 150.4, 149.8, 144.0, 143.6, 143.4 (C_{qpz}), 106.7, 106.6, 105.3 (CH_{pz}), 31.6 ($^1J_{CH}$ = 126 Hz, CH_2CH_3), 19.2 ($^1J_{CH}$ = 123 Hz, CH_2CH_3), 15.4, 15.0, 14.1, 14.0, 12.7, 12.5 (Me_{pz}), −2.6 ($^1J_{CH}$ = 126 Hz, Ir−CH_2). IR (nujol): ν(Ir−H) 2162, ν(CO) 2003 cm^{-1}. Anal. Calcd for $C_{19}H_{30}BN_6OIr$: C, 41.6; H, 5.5; N, 15.3. Found: C, 41.4; H, 5.0; N, 14.7.

X-ray Crystal Structure Analyses. X-ray data of complexes **4b**, **6b**, **7b**, and **8-Cl** (as solvate **8-Cl**·Et_2O) were collected on a Bruker Smart APEX CCD system or a Bruker-Nonius X8kappa APEX II CCD system (for **7b**) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space with θ_{max} = 30−30.6°. After data integration with the program SAINT+ corrections for absorption, $\lambda/2$ effects, and crystal decay were applied with the program SADABS.[27] The structures were solved by direct methods, expanded by Fourier syntheses, and refined on F^2 with the program suite SHELX97.[28] All non-hydrogen atoms were refined anisotropically. Most H atoms were placed in calculated positions and thereafter treated as riding. A torsional parameter was refined for each pyrazole-bound methyl group. The hydride H atoms in **4b**, **6b**, and **7b** were refined in *x*,*y*,*z* and U_{iso}. Crystal data and experimental details are given in Table 1, and the molecular structures are shown in Figures 1−4 with selected geometric data reported in the captions. Further details are given in the Supporting Information.

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Supporting Information Available: Complete crystallographic data and technical details in CIF format for compounds **4b**, **6b**, **7b**, and **8-Cl**·Et_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Bruker programs: *SMART*, version 5.629; *SAINT+*, version 6.45; *SADABS*, version 2.10; *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2003.

(28) Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; Bruker AXS Inc.: Madison, WI, 1997.