# Generation of Metallacyclic Structures from the Reactions of Vinyl Ethers with a $Tp^{Me2}Ir^{III}$ Compound

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The vinyl ethers $CH_2$═CHOEt and $CH_2$═CHO$Pr^n$ react with the $Ir^{III}$ fragment [$Tp^{Me2}Ir(C_6H_5)_2$] [**1**; $Tp^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate] with the formation of unusual metallacyclic structures. Each of the ethers gives rise to three different metallacyclic units in complexes **2**−**4**. Compounds **2** are iridacyclopentenes that contain a chelating organic ligand with alkyl and carbene termini, {Ir[═C(OR)$CH_2$CH(OR)$CH_2$]} (R = Et, $Pr^n$), resulting from the C−C coupling of two molecules of the ether, following prior vinylic C−H activation in one of them. They readily eliminate a molecule of the respective alcohol, ROH, in an acid-catalyzed process that leads to metallacyclopenta-1,3-diene units in **4** {Ir[═C(OR)CH═CH$CH_2$]}. Complexes **3** have a more complex metallacyclic structure resulting from tridentate coordination of a formally dianionic ligand that possesses alkyl, alkoxide, and carbene functionalities. Generation of this ligand involves the participation of two molecules of the vinyl ether, with one of them undergoing $C_{vinyl}$−O bond cleavage. The metallacyclic units that define the molecular structures of **2**−**4** have been unequivocally characterized by X-ray crystallography.

## Introduction

Transition-metal-mediated activation of the C−H bonds of simple organic substances followed by the formation of new C−C bonds, provides the basis for the synthesis of complex chemical compounds from common starting materials.[1] C−H bond activation of alkanes is known to proceed with the formation of a $\sigma$ complex resulting from coordination of the C−H bond to an unsaturated metal center.[2] However, because the metal/C−H electronic interaction is very weak,[3] experimental study of the C−H activation proves difficult, converting the catalytic functionalization of methane and other saturated hydrocarbons into a major challenge.[4,5]

In contrast, C−H bond activation of unsaturated hydrocarbons has been known for many years, and important catalytic transformations have been discovered.[6] Metal coordination to unsaturated C−C bonds may facilitate C−H cleavage. Similarly, many examples of C−H bond activation of ethers, thioethers, amines, and related molecules that contain a donor atom have been disclosed.[7,8] As shown in **A** for a methyl ether, coordination of the heteroatom allows the C−H bond to be activated to reach the metal coordination environment. Likewise, oxygen coordination assists cleavage of unstrained C−O bonds, a

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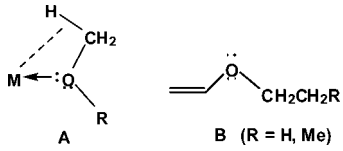
reaction relevant to hydrodeoxygenation of crude oil,[9] for which mechanistic information is sparse.[10−13]



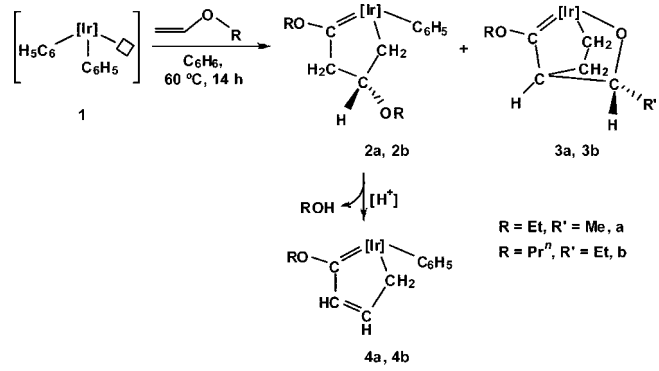

We showed recently that aliphatic ethers MeOBu$^t$, MeOBu$^n$, and MeOCH$_2$CH$_2$OMe react with the unsaturated fragment [Tp$^{Me2}$Ir(C$_6$H$_5$)$_2$] [**1**; Tp$^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate] to give hydride−carbene products,[14] in a complex process in which C−H bond rupture is accompanied by C−C bond formation. Extension of these results to vinyl ethers is of interest because vinylic or aliphatic C−H bond activation could, in principle, result. Vinyl ethers are important vinyl−oxygen compounds that can be regarded as derivatives of the hypothetical vinyl alcohol, the enol form of acetaldehyde. Together with other vinyl−oxygen compounds like vinyl esters, they find use as valuable monomers in polymer synthesis and are intermediates in low-temperature combustion processes.[15]

In this paper, we study the activation of the vinyl ethers **B** by the iridium fragment **1**. The two ethers behave similarly, each giving rise to three unusual metallacyclic structures, compounds **2**−**4**, whose generation implies C−H and C−O bond cleavage, as well as the formation of new C−C bonds. The three structural units that define the nature of **2**−**4** have been unequivocally characterized by X-ray crystallography, employing complexes **2a**, **3b**, and **4a** (see below) as representative examples.

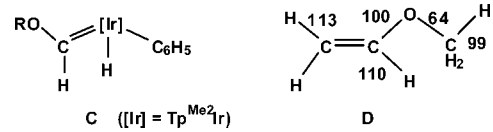
## Results and Discussion

It has previously been shown that the iridium-assisted C−H activation of methyl ethers MeOR, where R = CMe$_3$, CH$_2$CH$_2$CH$_2$CH$_3$, and CH$_2$CH$_2$OMe (see structure **A**) occurs in a regioselective manner with rupture of two α-C−H bonds of the Me group of the ether and formation of alkoxycarbenes of type **C**.[14] C−H cleavage at the adjacent methylene site

**Scheme 1**




MeO*CH*$_2$− does not occur, possibly because of a combination of two factors: higher steric hindrance and a preference for the formation of the stronger Ir−primary C bond.[16] On these grounds, the analogous activation of vinyl ethers **B** can be expected to occur with C−H activation at the α-vinylic carbon, despite the larger bond dissociation energy of this bond in comparison with the aliphatic C−H bonds (structure **D** shows calculated bond dissociation energies in kilocalories per mole for different bonds of methyl vinyl ether[15a]). This activation should be favored thermodynamically (Ir−alkenyl bonds are significantly stronger than Ir−alkyl bonds[17]) and also kinetically because both oxygen and C=C coordination to iridium could assist this reactivity.




As depicted in Scheme 1, fragment **1** generated *in situ* from Tp$^{Me2}$Ir(C$_2$H$_4$)$_2$ and C$_6$H$_6$ (60 °C, N$_2$ atmosphere) or Tp$^{Me2}$Ir(C$_6$H$_5$)$_2$(N$_2$)[18,19] reacts with CH$_2$=CHOR (R = Me, Pr$^n$) at 60 °C, over a period of 14 h, giving a mixture of two cyclic products **2a,b** and **3a,b** (**a** is used to label products derived from CH$_2$=CHOEt, whereas **b** marks derivatives of CH$_2$=CHOPr$^n$). The two ethers provide related compounds; their reaction products differenciate solely in the C atoms of the alkyl chain, R. Compounds **2** are iridacyclopentenes that contain a chelating organic ligand with alkyl and carbene termini, {Ir[=C(OR)CH$_2$CH(OR)CH$_2$]} (R = Et, Pr$^n$), while complexes **3** have a more complex metallacyclic structure resulting from tridentate coordination of a formally dianionic ligand that possesses alkyl, alkoxide, and carbene functionalities. The reaction of Scheme 1 is routinely effected, utilizing 20 equiv of the corresponding ether. Under these conditions, $^1$H NMR monitoring reveals a spectroscopic yield close to 80%, with **2** and **3** forming in an approximate 1:3 ratio. The use of 100 equiv of the ether introduces little variation except a small increase of the **2**/**3** proportion. Because isolated samples of **2** and **3**, heated in the presence of the corresponding ether under conditions identical with those in Scheme 1, do not interconvert,

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it is clear that the two compounds form through different reaction pathways.

Compounds **2** and **3** can be separated by column chromatography (see the Experimental Section), but while **3** remains unaltered during this segregation procedure, **2** converts partially into a new iridacycle product, **4**, having metallacyclopenta-1,3-diene units {Ir[=C(OR)$CH_2$CH(OR)$CH_2$]}. Once again, **2a** and **2b** exhibit similar behavior, with their conversion into **4a** and **4b**, respectively, requiring elimination of a molecule of the corresponding alcohol, EtOH or Pr$^n$OH. In fact, compounds **4** are best obtained by the acid-catalyzed elimination of a molecule of ROH from precursors **2** (see the Experimental Section).

Microanalyses and extensive 1D and 2D NMR studies, summarized in the Experimental Section, provide unequivocal support for the molecular complexity of compounds **2**−**4**, as is shown in Scheme 1. Molecules of the new compounds are chiral at the metal. Furthermore, complexes **2a** and **2b** contain a stereogenic C atom, while bicyclic derivatives **3a** and **3b** have two asymmetrically substituted C atoms. Despite this structural complexity and the reasonable expectation of different stereoisomers, NMR spectroscopy reveals the formation of only one diastereoisomer in each case (NOESY experiments are in accordance with the stereochemistry shown in Scheme 1, and this has been further demonstrated by the X-ray studies discussed below).

The lack of symmetry of these molecules results in the expected complexity of their NMR spectra. For instance, the H atoms of the four $CH_2$ groups of **2a** are diastereotopic. The methylene group directly bonded to iridium gives rise to $^1$H NMR signals at 3.45 and 3.21 ppm (dd, dd, $^2J_{HH}$ = 11.4 Hz; $^3J_{HH}$ = 6.9 and 9.5 Hz) and to a $^{13}$C{$^1$H} NMR peak at 6.9 ppm. In the $^{13}$C{$^1$H} NMR spectrum, the iridium-bound carbene C atom appears in the proximity of 265 ppm for the monocyclic species **2a** and **2b** and around 278 ppm for bicyclic derivatives **3a** and **3b**. Finally, complexes **4a** and **4b** display NMR spectra that are also in accordance with the depicted structures. For instance, the iridacyclopentadiene unit of **4a** features two characteristic doublets of triplets at 2.58 and 1.64 ppm ($^2J_{HH}$ = 20.4 Hz; $^3J_{HH}$ and $^4J_{HH}$ = 2.1 Hz) in the $^1$H NMR spectrum, due to methylenic protons, and two multiplets at 8.27 ppm (dt, $^3J_{HH}$ = 6.0, 2.1, and 2.1 Hz) and 6.95 ppm (dt, $^3J_{HH}$ = 6.0 Hz; $^4J_{HH}$ = 2.1 Hz) attributable to the olefinic hydrogen nuclei. The corresponding $^{13}$C{$^1$H} NMR resonances are registered at 13.0 (Ir−$CH_2$), 143.8, and 183.3 ppm. The latter two are due to the CH= nuclei and have $^1J_{CH}$ values of 157 and 151 Hz, respectively. The carbene C atom of this metallacyclic unit resonates at 257.7 ppm.

Figures 1−3 collect ORTEP diagrams for complexes **2a**, **3b**, and **4a**, respectively, and include atom numbering schemes as well as important bond lengths and angles. Relevant structure data for the three compounds are compiled in Table 1. As was already commented on, compounds **2** feature iridacyclopentene structures, with a Fischer carbene unit being responsible for the ring unsaturation, while complexes **4** are iridacyclopenta-1,3-dienes, once more with a carbene functionality. Compounds **3** are also Fischer carbenes but display a more complex bicyclic structure that results from tridentate coordination of a new, formally dianionic ligand, consisting of alkyl, alkoxide, and carbene termini. The organometallic bidentate ligand of **2** has iridium-bound alkyl and carbene units, derives from C−C coupling of two molecules of the vinyl ether, and readily eliminates ROH from substituents at C2 and C3 to generate the iridacyclopentadiene moiety that characterizes complexes **4**. The formation of compounds **3** also requires participation of

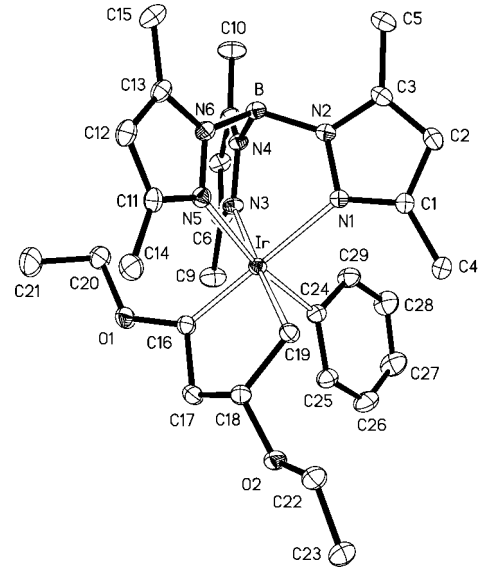



**Figure 1.** X-ray structure of complex **2a** (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ir−C16 1.897(2), Ir−C19 2.091(2), Ir−C24 2.062(2), Ir−N1 2.179(2), Ir−N3 2.168(2), Ir−N5 2.180(2), C16−C17 1.514(3), C17−C18 1.522(3), C18−C19 1.537(3), C16−O1 1.321(3), C18−O2 1.433(3); N1−Ir−N3 86.6(1), N1−Ir−N5 83.1(1), N3−Ir−N5 87.5(1).

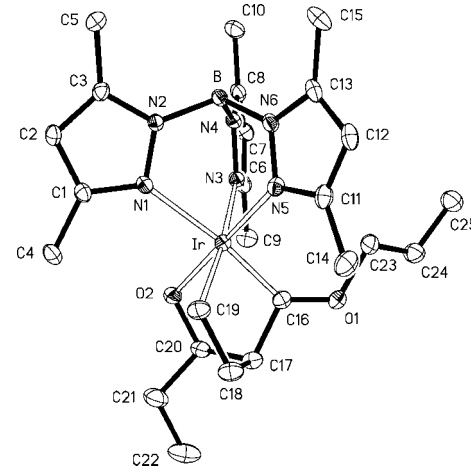



**Figure 2.** X-ray structure of complex **3b** (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ir−C16 1.881(2), Ir−C19 2.081(2), Ir−O2 2.039(2), Ir−N1 2.156(2), Ir−N3 2.177(2), Ir−N5 2.063(2), C16−C17 1.507(3), C17−C18 1.538(4), C18−C19 1.545(3), C17−C20 1.552(4), C20−O2 1.414(3), C20−C21 1.518(4), C16−O1 1.319(3); N1−Ir−N3 82.4(1), N1−Ir−N5 87.7(1), N3−Ir−N5 88.3(1), C16−Ir−C19 82.2(1), C16−Ir−O2 81.5(1), C19−Ir−O2 82.1(1).

two molecules of the vinyl ether, which, nevertheless, react in a more complex manner. Indeed, in addition to C−H bond activation, cleavage of the vinylic =CH−O− bond of one ether molecule is needed, along with the formation of two C−C bonds. It is pertinent to remark that, despite the large difference that exists in the bond dissociation energies of the two C−O bonds (more than 35 kcal mol$^{-1}$ in $CH_2$=CHOMe[15a]), it is the stronger =CH−O− bond that breaks in the reaction.

In the three structurally characterized compounds, the Ir−C bond to the heteroatom-substituted carbene ligand has a length close to 1.90 Å, a value comparable to that found in other iridium(III) carbenes.[8,19,20] This bond length is shorter than the Ir−C(sp$^3$) separations (ca. 2.08 Å) and also than the Ir−C(sp$^2$)

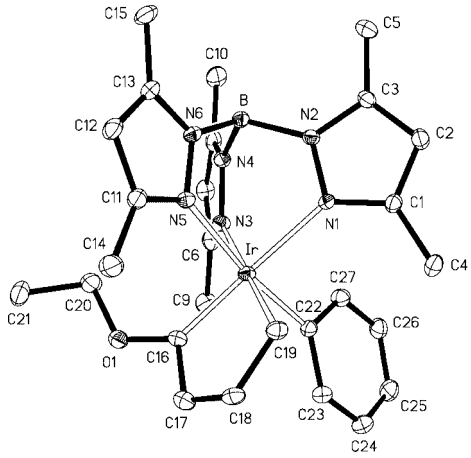



**Figure 3.** ORTEP representation of complex **4a** (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ir−C16 1.918(2), Ir−C19 2.088(2), Ir−C22 2.066(2), Ir−N1 2.170(2), Ir−N3 2.153(2), Ir−N5 2.161(2), C16−C17 1.464(3), C17−C18 1.335(3), C18−C19 1.495(3), C16−O1 1.336(3); N1−Ir−N3 86.0(1), N1−Ir−N5 85.2(1), N3−Ir−N5 86.9(1), C16−Ir−C19 80.8(1).

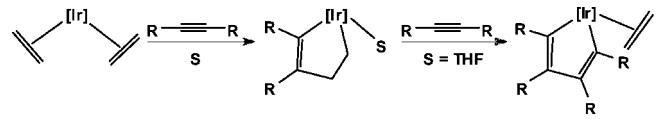
**Table 1. Crystal Data and Data Collection and Refinement Details for 2a, 3b, and 4a**

| | **2a**[c] | **3b** | **4a** |
|---|---|---|---|
| formula | $C_{29}H_{42}BIrN_6O_2$ | $C_{25}H_{40}BIrN_6O_2$ | $C_{27}H_{36}BIrN_6O$ |
| mol wt | 709.70 | 659.64 | 663.63 |
| color, habit | orange, prism | orange, block | orange, blade |
| symmetry, space group | monoclinic, $P2_1/n$ | triclinic, $P\bar{1}$ | monoclinic, $P2_1/n$ |
| $a$, Å | 11.2010(5) | 8.0223(4) | 8.0575(4) |
| $b$, Å | 17.6163(8) | 13.1372(6) | 20.3891(11) |
| $c$, Å | 16.7825(8) | 13.2581(6) | 16.4221(9) |
| α, deg | 90 | 97.230(1) | 90 |
| $\beta$, deg | 94.928(1) | 94.549(1) | 104.086(1) |
| $\gamma$, deg | 90 | 96.359(1) | 90 |
| $V$, Å$^3$ | 3299.3(3) | 1371.46(11) | 2616.8(2) |
| $Z$ | 4 | 2 | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.429 | 1.597 | 1.684 |
| $\mu$, mm$^{-1}$ | 4.080 | 4.900 | 5.134 |
| $\theta$ range, deg | 2.1−30.0 | 2.4−30.0 | 2.4−30.0 |
| temp, K | 297(2) | 173(2) | 100(2) |
| no. of data collected | 42 341 | 31 122 | 48 174 |
| no. of unique data | 9525 ($R_{int}$ = 0.020) | 7970 ($R_{int}$ = 0.026) | 7595 ($R_{int}$ = 0.026) |
| no. of param/ restraints | 361/0 | 322/0 | 331/0 |
| R1[a] [$F^2 > 2\sigma(F^2)$] | 0.0195 | 0.0210 | 0.0217 |
| wR2[b] (all data) | 0.0509 | 0.0497 | 0.0452 |

[a] $R1(F) = F_o - F_cF_o$. [b] $wR2(F^2) = \{[w(F_o^2 - F_c^2)^2]/[(w(F_o^2)^2]\}^{1/2}$. [c] Crystalline **2a** is a disordered solvate of $CH_2Cl_2$/pentane. This solvent is not contained in chemical formulas or quantities derived thereof.

bond to the phenyl group of **2a** and **4a** (2.06 Å). It should also be mentioned that the C−O bond that the carbene C atoms form in the three complexes, of ca. 1.32 Å, is appreciably shorter than the other O−C bond that this O atom forms with the ethyl (**2a** and **4a**) or *n*-propyl groups (**3b**), of approximately 1.46 Å. Accordingly, some multiple-bond character exists within the {Ir[=C(OR)$CH_2$CH(OR)$CH_2$]} unit of these complexes, as would actually be anticipated for Fischer carbenes.[21] The

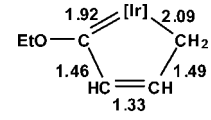
**Scheme 2**




[Ir] = TpIr; R = $CO_2Me$; S = NCMe, THF

structural parameters just discussed match closely those we have found recently in related iridium(III) alkoxycarbenes.[14] Interestingly, while in **2a** and **4a** the three Ir−N distances to the $Tp^{Me2}$ ligand are identical within experimental error, with a value of ca. 2.16 Å, in the bicyclic derivative **3b**, the Ir−N5 bond (Figure 2), which is trans to the alkoxide terminus, i.e., trans to O2, is shorter than the other two by ca. 0.1 Å. These observations suggest that the carbene and hydrocarbyl ligands of these molecules have similar trans influence, which is, however, somewhat larger than that of the alkoxide group of **3b**.

To close this section, some comments on the iridacyclic linkages of **2**−**4** are worthy of note. Metallacyclopentene and metallacyclopentadiene derivatives of the transition elements have been intensively studied as important intermediates for the cyclooligomerization of alkynes.[22,23] Tp′Ir compounds in which the metal is part of an unsaturated five-membered ring are known.[22a,b,24] An interesting observation by O'Connor and coworkers is the conversion of an iridacyclopentene complex into an iridacyclopentadiene−alkene complex (Scheme 2).[24] While this 2,4-metallacyclopentadiene group is a relatively common, well-known structural motif, metallacyclopenta-1,3-dienes of type **4** are much rarer[25] and, to our knowledge, are unknown for iridium. Structure **E** represents the unsaturated metallacyclic moiety of **4a** and includes Ir−C and C−C bond distances within the ring that suggests some alternation in double-bond character, but attempts to deprotonate its methylene group by treatment of **4a** with LiBu$^n$ have proved fruitless.




**E**

Scheme 3 presents a reasonable reaction pathway that leads to the formation of compounds **2** and **4**. The reaction starts with α-vinylic C−H activation, possibly assisted by coordination to the O atom of the ether (or to the C=C bond), and elimination of a molecule of benzene. In accordance with theoretical

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

(20) (a) Werner, H.; Werber, B.; Nürnberg, O.; Wolf, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1025. (b) Clark, G. R.; Roger, W. R.; Wright, A. H. *J. Organomet. Chem.* **1982**, *236*, C7.

(21) See, for example, p 338 of ref 6a.

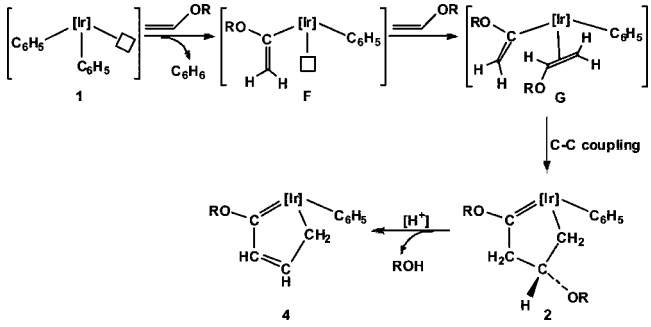
(22) (a) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Álvarez, E.; Mereiter, K. *Chem.−Eur. J.* **2007**, *13*, 5160. (b) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendon, N.; Mereiter, K. *Organometallics* **2007**, *26*, 3120. (c) Gandon, V.; Agenet, N.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2006**, *128*, 8509. (d) Nishiyama, H.; Niwa, E.; Inoue, T.; Ishima, Y.; Aoki, K. *Organometallics* **2002**, *21*, 2572.

(23) General reviews of alkyne cyclotrimerization:(a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Shore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1129. (c) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 741. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635. (e) Malacria, M. *Chem. Rev.* **1996**, *96*, 289. (f) Bönnemann, H.; Brijoux, W. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 114.

(24) O'Connor, J. M.; Closson, A.; Gantzel, P. *J. Am. Chem. Soc.* **2002**, *124*, 2434.

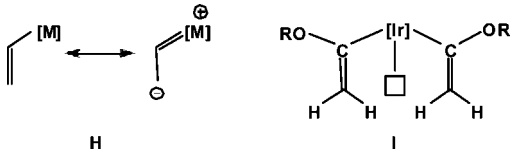
(25) (a) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810. (b) Herberich, G. E.; Mayer, H. *Organometallics* **1990**, *9*, 2655. (c) Yeh, W. Y.; Peng, S. M.; Liu, L. K. *Inorg. Chem.* **1993**, *32*, 2965.

**Scheme 3**



calculations on the related C−H bond activation of alkyl aryl ethers to be discussed elsewhere, it is likely that C−H cleavage occurs in a concerted manner, with the formation of a $\sigma$-C−H complex, that is, through a $\sigma$-CAM mechanism.[2b] The resulting alkenyl derivative (**F** in Scheme 3) could coordinate another molecule of the ether to give **G**, which can then experience nucleophilic attack of the $\beta$-alkenyl C atom onto the α-C of the vinyl moiety. This alkenyl nucleophilic reactivity can be attributed to the important contribution of the dipolar canonical form to the resonance hybrid **H**.[26]

With respect to the bicyclic complexes **3**, the mechanism that directs their formation has to be necessarily complex. It is reasonable to suggest that a bis(alkenyl) species **I** could be initially formed by stepwise C−H activation of two molecules of the ether, and this could be followed by α-OR elimination, leading to an alkenyl−alkoxide−vinylidene intermediate. A complex reaction pathway may be envisaged to explain generation of metallabicycles **3**, and while this pathway consists of familiar, elementary organometallic reactions, we believe that in the absence of mechanistic information further discussion is unjustified.



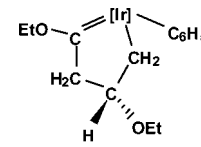
## Conclusions

To conclude, novel, interesting metallacyclic structures can be generated under moderate conditions during the activation of the vinyl ethers $CH_2$=CHOEt and $CH_2$=CHOPr$^n$ by the unsaturated iridium fragment **1**. Two molecules of the ether participate in the reaction that progresses through two independent, competitive pathways, leading respectively to complexes **2** and **3**. Spectroscopic and X-ray studies reveal that compounds **2** are iridacyclopentenes, unsaturated at the carbene terminus of the chelating hydrocarbyl ligand, and result from C−C coupling of the two ether molecules. A very facile, acid-catalyzed, process eliminates a molecule of the corresponding alcohol, yielding iridacyclopenta-1,3-dienes **4**. In turn, complexes **3** have a bimetallacyclic structure and result from a complex reaction where C−H and C−O cleavage, as well as the formation of two C−C bonds, take place.

(26) (a) Alías, F. M.; Daff, P. J.; Paneque, M.; Poveda, M. L.; Carmona, E.; Pérez, P. J.; Salazar, V.; Alvarado, Y.; Atencio, R.; Sánchez-Delgado, R. *Chem.—Eur. J.* **2002**, *8*, 5132. (b) 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. (c) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951. (d) Zhen, H.; Wang, C.; Hu, Y.; Flood, T. C. *Organometallics* **1998**, *17*, 5397.

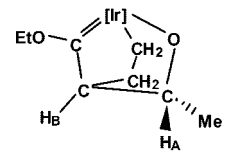
## Experimental Section

**General Procedures.** Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (0 ppm) using the residual protiosolvent peaks as internal standards ($^1$H NMR experiments) or the characteristic resonances of the solvent nuclei ($^{13}$C NMR experiments). Spectral assignments were made by means of routine 1D and 2D NMR experiments where appropriate. The coupling constants $^1J_{CH}$ were measured by $^{13}$C GATED experiments. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(C_2H_4)_2$[18] and $Tp^{Me2}Ir(C_6H_5)_2(N_2)$[19] were obtained by published procedures.



**2a**

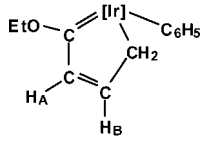
**Complex 2a.** Compound $Tp^{Me2}Ir(C_2H_4)_2$ (0.20 g, 0.37 mmol) dissolved in $C_6H_6$ (12 mL) was treated with ethyl vinyl ether (0.7 mL, 7.3 mmol), and the resulting solution was stirred for 14 h at 60 °C. The solvent was then removed under vacuo, and NMR monitoring of the crude product revealed the formation of a mixture of **2a** and **3a** (ca. 1:3). Separation was achieved by column chromatography on silica gel (30:1 → 0:100; hexane/$Et_2O$) to yield 15% (0.036 g) of pure **2a**. Separation by column chromatography must be carried out quickly because **2a** transforms into **4a** during this operation. Compound **2a** can be crystallized by cooling its solutions to −20 °C in a mixture of pentane and $CH_2Cl_2$. $R_f$ = 0.54 [silica gel, hexane/$Et_2O$ (5:1)]. $^1$H NMR ($CDCl_3$): $\delta$ 8.00, 7.09, 6.76, 6.51, 5.92 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx$ 7.5 Hz, 5 $CH_{ar}$), 5.77, 5.73, 5.59 (s, 1 H each, 3 $CH_{pz}$), 4.69 (multiplet, 1 H, $^3J_{HH}$ = 7.7 Hz, Ir−$CH_2$C*H*OR), 3.86, 3.70 (dq, m, 1 H each, $^2J_{HH}$ = 10.6 Hz, $^3J_{HMe}$ = 7.2 Hz, Ir−$CH_2$CH−OC*H*$_2$CH$_3$), 3.80, 3.56 (dq, dq, 1 H each, $^2J_{HH}$ = 9.2 Hz, $^3J_{HMe}$ = 6.9 and 6.9 Hz, respectively, Ir=C−OC*H*$_2$CH$_3$), 3.45, 3.21 (dd, dd, 1 H each, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 6.9 and 9.5 Hz, respectively, Ir−$CH_2$), 3.38, 2.59 (dd, dd, 1 H each, $^2J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 8.0 and 7.7 Hz, respectively, Ir=C−C*H*$_2$), 2.45, 2.41, 2.37, 2.00, 1.48, 1.41 (s, 3 H each, 6 $Me_{pz}$), 1.33 (t, 3 H, Ir=C−OCH$_2$C*H*$_3$), 1.07 (t, 3 H, Ir−CH−OCH$_2$C*H*$_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 265.0 (Ir=C), 152.9, 149.8, 148.8, 144.1, 143.0, 142.7 ($C_{qpz}$), 140.2, 136.6, 125.5, 125.2, 120.9 ($CH_{ar}$), 136.2 ($C_{qar}$), 107.9, 106.9, 106.3 ($CH_{pz}$), 83.7 ($^1J_{CH}$ = 138 Hz, IrCH$_2$*C*H−O), 71.0 ($^1J_{CH}$ = 148 Hz, IrCH$_2$CH−O*C*H$_2$CH$_3$), 66.2 ($^1J_{CH}$ = 122 Hz, Ir=C−*C*H$_2$), 64.1 ($^1J_{CH}$ = 139 Hz, Ir=C−O*C*H$_2$CH$_3$), 15.9 (Ir=C−OCH$_2$*C*H$_3$), 14.9 (IrCH$_2$CH−OCH$_2$*C*H$_3$), 14.9, 14.8, 13.4, 13.1, 12.8, 12.8 ($Me_{pz}$), 6.9 ($^1J_{CH}$ = 126 Hz, Ir−$CH_2$). Anal. Calcd for $C_{29}H_{42}BN_6O_2Ir \cdot 0.25C_5H_{12}$: C, 49.9; H, 6.2; N, 11.5. Found: C, 49.7; H, 6.2; N, 11.2.



**3a**

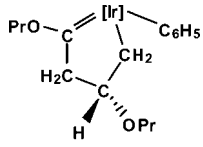
**Complex 3a.** This compound was generated by the method described above for complex **2a**. Yield: 30%. A sample of analytical purity was obtained by cooling a solution of **3a** at −20 °C in a mixture of pentane and $CH_2Cl_2$. $R_f$ = 0.25 [silica gel, $Et_2O$]. $^1$H NMR ($CDCl_3$): $\delta$ 5.71, 5.70, 5.68 (s, 1 H each, 3 $CH_{pz}$), 4.63 (m,

1 H, $H_A$), 4.07, 3.87 (dq, dq, 1 H each, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.2 Hz, $-OCH_2CH_3$), 3.54, 2.84 (q, m, 1 H each, $^2J_{HH}$ = $^3J_{HH}$ = 9.5 Hz, $IrCH_2CH_2$), 2.81 (m, 1 H, $H_B$), 2.41, 2.23 (m, m, 1 H each, $IrCH_2CH_2$), 2.82, 2.39, 2.34, 2.30, 2.14, 2.11 (s, 3 H each, 6 $Me_{pz}$), 1.48 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, $CH_AMe$), 1.31 (t, 3 H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 278.2 (Ir=C), 153.3, 149.7, 148.2, 143.8, 143.1, 142.7 ($C_{qpz}$), 107.9, 106.5, 105.5 ($CH_{pz}$), 81.4 ($^1J_{CH}$ = 131 Hz, $CH_B$), 78.5 ($^1J_{CH}$ = 132 Hz, $CH_A$), 73.6 ($^1J_{CH}$ = 148 Hz, $-OCH_2CH_3$), 31.2 ($^1J_{CH}$ = 127 Hz, $IrCH_2CH_2$), 19.5 ($^1J_{CH}$ = 127 Hz, $CH_AMe$), 14.4, 14.0, 13.7, 13.3, 13.1, 12.5, 12.4 (6 $Me_{pz}$ + $-OCH_2CH_3$), −6.97 ($^1J_{CH}$ = 129 Hz, $IrCH_2CH_2$). Anal. Calcd for $C_{23}H_{36}BN_6OIr\cdot CH_2Cl_2$: C, 41.1; H, 5.4; N, 12.0. Found: C, 41.0; H, 5.3; N, 11.9.



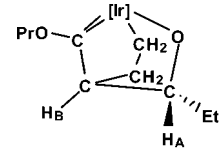

4a

**Complex 4a.** (a) Following generation of the mixture of complexes **2a** and **3a**, as described previously, compound **2a** was found to transform into **4a** during separation by column chromatography when **2a** was kept in the column for a period of more than 14 h (15% yield). Complex **4a** was crystallized from pentane/$Et_2O$ mixtures (2:1) at −20 °C. (b) Compound **2a** (0.020 g, 0.028 mmol) was dissolved in THF (2 mL), and 37% HCl (0.05 mL) was added. Instantly, the solution turned from yellow to red. The solvent was removed under reduced pressure and quantitative conversion into **4a** was ascertained by $^1H$ NMR. $R_f$ = 0.35 [silica gel, hexane/$Et_2O$ (10:1)]. $^1H$ NMR ($CDCl_3$): $\delta$ 8.27 (dt, 1 H, $^3J_{BA}$ = 6.0 Hz, $^3J_{HH}$ = 2.1 Hz, $H_B$), 6.95 (dt, 1 H, $^4J_{HH}$ = 2.1 Hz, $H_A$), 7.09, 6.83, 6.68, 6.53, 6.02 (dt, td, tt, td, dt, 1 H each, $^3J_{HH} \approx$ 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, 5 $CH_{ar}$), 5.76, 5.67, 5.65 (s, 1 H each, 3 $CH_{pz}$), 4.26 (multiplet, AB part of an $ABX_3$ spin system, $^3J_{HH}$ = 7.1 Hz, $J_{ap}$ = 0.9 Hz, $-OCH_2CH_3$), 2.58, 1.64 (dt, dt, 1 H each, $^2J_{HH}$ = 20.4 Hz, $^3J_{HH}$ = $^4J_{HH}$ = 2.1 Hz, $Ir-CH_2$), 2.46, 2.41, 2.38, 1.77, 1.61, 1.47 (s, 3 H each, 6 $Me_{pz}$), 1.26 (t, 3 H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 257.7 (Ir=C), 183.3 ($^1J_{CH}$ = 151 Hz, $CH_B$), 152.4, 151.3, 150.4, 143.5, 142.9, 142.5 ($C_{qpz}$), 143.8 ($^1J_{CH}$ = 157 Hz, $CH_A$), 139.7, 132.5, 125.7, 124.5, 120.7 ($CH_{ar}$), 134.4 ($C_{qar}$), 107.7, 107.2, 106.6 ($CH_{pz}$), 69.1 ($^1J_{CH}$ = 150 Hz, $-OCH_2CH_3$), 15.2 ($-OCH_2CH_3$), 13.0 ($Ir-CH_2$), 14.8, 13.9, 13.8, 13.0, 12.9, 12.8 ($Me_{pz}$). Anal. Calcd for $C_{27}H_{36}BN_6O_2Ir$: C, 48.9; H, 5.4; N, 12.7. Found: C, 48.6; H, 5.5; N, 12.4.



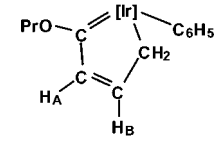

2b

**Complex 2b.** This compound was prepared similarly to **2a** using a solution of $Tp^{Me2}Ir(C_2H_4)_2$ in $C_6H_6$ (0.20 g, 0.37 mmol; 10 mL) and propyl vinyl ether (0.7 mL, 6.2 mmol). A pale-orange solution was obtained that upon removal of the volatiles under vacuum converted into a crude solid consisting of a ca. 1:2 mixture of **2b/3b** ($^1H$ NMR). Separation of the two compounds by column chromatography on silica gel (30:1 → 1:5; hexane/$Et_2O$) gave 0.04 g of **2a** (15%). $R_f$ = 0.37 [silica gel, hexane/$Et_2O$ (5:1)]. $^1H$ NMR ($CDCl_3$): $\delta$ 8.06, 7.07, 6.75, 6.50, 5.94 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx$ 7.5 Hz, 5 $CH_{ar}$), 5.75, 5.72, 5.58 (s, 1 H each, 3 $CH_{pz}$), 4.66 (multiplet, 1 H, $^3J_{HH}$ = 7.8 Hz, $Ir-CH_2CHO$), 3.70, 3.47 (m, m, 1 H each, $Ir-CH_2CH-OCH_2CH_2CH_3$), 3.68, 3.45 (m, m, 1 H each, $Ir=C-OCH_2CH_2CH_3$), 3.46, 3.23 (m, dd, 1 H each, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 10.0 Hz, $Ir-CH_2$), 3.38, 2.58 (dd, dd, 1 H each, $^2J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 7.5 and 7.8 Hz, respectively, $Ir=C-CH_2$), 2.45, 2.40, 2.36, 1.98, 1.47, 1.40 (s, 3 H each, 6 $Me_{pz}$), 1.72 (m, 2 H, $-OCH_2CH_2CH_3$), 1.46, 1.39 (m, m, 1 H each, $-OCH_2CH_2CH_3$), 1.05 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $-OCH_2CH_2CH_3$), 0.87 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $-OCH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 265.3 (Ir=C), 152.8, 149.8, 148.8, 144.0, 143.0, 145.6 ($C_{qpz}$), 140.2, 136.8, 125.4, 125.2, 120.9 ($CH_{ar}$), 136.3 ($C_{qar}$), 107.9, 106.9, 106.2 ($CH_{pz}$), 83.7 ($^1J_{CH}$ = 139 Hz, $IrCH_2CH-O$), 76.6 ($^1J_{CH}$ = 149 Hz, $IrCH_2CH-OCH_2CH_2CH_3$), 70.7 ($^1J_{CH}$ = 136 Hz, $Ir=C-OCH_2CH_2CH_3$), 66.3 ($^1J_{CH}$ = 125 Hz, $Ir=C-CH_2$), 23.5, 22.5 ($-OCH_2CH_2CH_3$), 14.9, 14.9, 13.3, 13.0, 12.8, 12.7 ($Me_{pz}$), 11.1, 10.1 ($-OCH_2CH_2CH_3$), 7.1 ($^1J_{CH}$ = 129 Hz, $Ir-CH_2$). Anal. Calcd for $C_{31}H_{46}BN_6O_2Ir$: C, 50.4; H, 6.2; N, 11.4. Found: C, 49.7; H, 6.4; N, 11.1.




3b

**Complex 3b.** This complex was obtained by the method reported for **2b**. Yield: 25%. Compound **3b** was crystallized from pentane/$CH_2Cl_2$ at −20 °C. $R_f$ = 0.21 [silica gel, hexane/$Et_2O$ (10:1)]. $^1H$ NMR ($CDCl_3$): $\delta$ 5.71, 5.68 (s, 2:1, 3 $CH_{pz}$), 4.30 (m, 1 H, $H_A$), 3.94, 3.73 (dt, dt, 1 H each, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 6.4 Hz, $-OCH_2CH_2CH_3$), 3.52, 2.80 (q, m, 1 H each, $^2J_{HH}$ = $^3J_{HH}$ = 9.2 Hz, $IrCH_2CH_2$), 2.93 (m, 1 H, $H_B$), 2.82, 2.39, 2.34, 2.30, 2.14, 2.11 (s, 3 H each, 6 $Me_{pz}$), 2.37, 2.23 (m, m, 1 H each, $IrCH_2CH_2$), 1.93 (m, 2 H, $CH_ACH_2$), 1.67 (m, 2 H, $-OCH_2CH_2CH_3$), 0.93 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, $CH_ACH_2CH_3$), 0.89 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, $-OCH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 278.2 (Ir=C), 153.3, 149.7, 148.2, 143.8, 143.2, 142.7 ($C_{qpz}$), 108.0, 106.4, 105.6 ($CH_{pz}$), 84.8 ($^1J_{CH}$ = 139 Hz, $CH_A$), 79.3 ($CH_B$), 78.8 ($-OCH_2CH_2CH_3$), 31.5 ($^1J_{CH}$ = 130 Hz, $IrCH_2CH_2$), 27.6 ($^1J_{CH}$ = 132 Hz, $CH_ACH_2$), 22.2 ($^1J_{CH}$ = 126 Hz, $-OCH_2CH_2CH_3$), 14.1, 13.7, 13.3, 13.0, 12.4 (1:1:1:1:2, $Me_{pz}$), 12.1 ($^1J_{CH}$ = 127 Hz, $-CH_ACH_2CH_3$), 10.8 ($^1J_{CH}$ = 127 Hz, $-OCH_2CH_2CH_3$), −6.8 ($^1J_{CH}$ = 131 Hz, $IrCH_2CH_2$). Anal. Calcd for $C_{23}H_{36}BN_6OIr\cdot 0.25\ CH_2Cl_2$: C, 45.6; H, 6.1; N, 12.6. Found: C, 45.4; H, 5.9; N, 12.4.




4b

**Complex 4b.** Compound **2b** (0.015 g, 0.020 mmol) was dissolved in THF (3 mL), and 20% HCl (0.05 mL) was added. The mixture was stirred at 60 °C for 30 min and the solvent removed under reduced pressure. Quantitative conversion into **4b** was ascertained by $^1H$ NMR. $^1H$ NMR ($CDCl_3$): $\delta$ 8.20 (dt, 1 H, $^3J_{BA}$ = 5.7 Hz, $^3J_{HH}$ = 2.7 Hz, $H_B$), 6.90 (d, 1 H, $H_A$), 7.09, 6.80, 6.65, 6.50, 6.00 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx$ 7.3 Hz, 5 $CH_{ar}$), 5.72, 5.65, 5.62 (s, 1 H each, 3 $CH_{pz}$), 4.06 (pseudo-qd, AB part of an $ABX_3$ spin system, $^3J_{HH}$ = 6.8 Hz, $J_{ap}$ = 1.0 Hz, $-OCH_2CH_2CH_3$), 2.58, 1.64 (dt, m, 1 H each, $^2J_{HH}$ = 20.5 Hz, $^3J_{HH}$ = $^4J_{HH}$ = 2.0 and 2.0 Hz, respectively, $Ir-CH_2$), 2.43, 2.38, 2.36, 1.74, 1.60, 1.41 (s, 3 H each, 6 $Me_{pz}$), 1.57 (m, 2 H, $-OCH_2CH_2CH_3$), 0.76 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $-OCH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 258.2 (Ir=C), 182.6 ($^1J_{CH}$ = 151 Hz, $CH_B$), 152.4, 151.2, 150.3, 143.5, 142.9, 142.4 ($C_{qpz}$), 144.2 ($^1J_{CH}$ = 165 Hz, $CH_A$), 139.7, 132.5, 125.7, 124.5, 120.7 ($CH_{ar}$), 134.4 ($C_{qar}$), 107.6, 107.1, 106.4 ($CH_{pz}$), 75.0 ($^1J_{CH}$ = 151 Hz, $-OCH_2CH_2CH_3$), 22.8 ($^1J_{CH}$ = 124 Hz, $-OCH_2CH_2CH_3$), 12.9 ($Ir-CH_2$), 14.8, 13.9, 13.7, 12.9, 12.9, 12.8 ($Me_{pz}$), 10.1 ($-OCH_2CH_2CH_3$).

**X-ray Crystal Structure Analyses.** X-ray data of complexes **2a** (as the solvate **2a**·solv crystallized from $CH_2Cl_2$/pentane), **3b**, and **4a** were collected on a Bruker Smart APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and 0.3° $\omega$-scan frames covering complete spheres of the reciprocal space with $\theta_{max} = 30°$. After data integration with program *SAINT+* corrections for absorption, $\lambda/2$ effects, and crystal decay were applied with program *SADABS*.[27] The structures were solved by direct methods (*SHELXS97*) and refined on $F^2$ with program *SHELXL97*.[28] All non-H 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 disordered solvent in **2a**·solv was squeezed with program *PLATON*.[29] Crystal data and experimental details are given in Table 1, and the molecular structures are shown in Figures 1−3, with selected geometric data reported in the captions.

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**Supporting Information Available:** Complete crystallographic data and technical details in CIF format for compounds **2a**, **3b**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800844X

(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*; University of Göttingen: Göttingen, Germany.

(29) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht, Utrecht, The Netherlands, 2008.