Intramolecular Oxygen Transfer from Nitro Groups to C≡C Bonds Mediated by Iridium Hydrides

Xingwei Li, Christopher D. Incarvito, Tiffany Vogel, and Robert H. Crabtree*

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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The functionalized alkynes *o*-RC≡C(C_6H_4)NO_2 (R = H or alkyl) formally insert into two iridium hydrides, during which O-transfer of the nitro group into the C≡C bond of *o*-RC≡C(C_6H_4)NO_2 is observed. For the terminal alkyne with R = H, iridium(III) nitroso complexes were isolated. For internal alkynes with R = Me or ^{n}Pr, iridium hydride anthranil complexes were obtained as a result of O-transfer with a different regiochemistry. Mechanisms for these transformations, including a previously unknown O-transfer step from the nitro to the RC≡C bond, are proposed.

1. Introduction

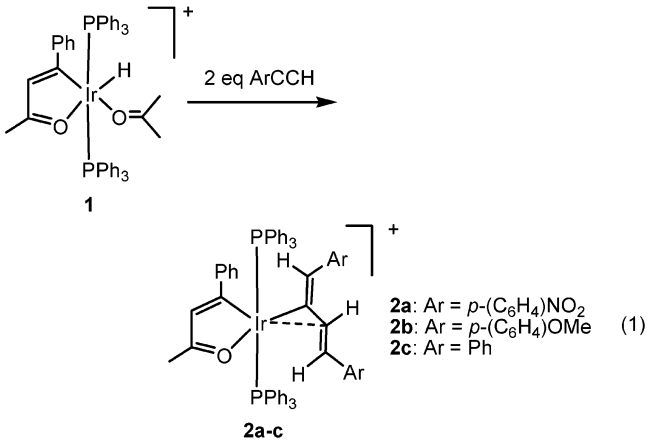
Readily available organic nitro compounds are rarely effective oxidants in organic transformations.[1] However, oxygen transfer from the nitro group in transition metal complexes M−NO_2 or organic nitro compounds can be mediated by transition metals, resulting in the oxidation of alkenes,[2] CO,[3] and phosphines[4] (Scheme 1). Oxygen transfer to CO has been extensively studied owing to its synthetic applications in carbamation,[3a,b,5] reductive N-heteroannulation,[6] and allyl amination.[7] As a result of the oxygen transfer, nitroso complexes are formed. The nitroso ligand could adopt η^1-N, η^1-O, and η^2-(N, O) binding modes, often distinguishable by IR spectroscopy.[8]

Previously known mechanisms (Scheme 2) for the O-transfer from nitro groups include nucleophilic attack of the nitro oxygen on the oxidizable group L (path (a)),[2b] where a more polarized L ligand will be more favorable, and outer (path (b)) or inner (path (c)) sphere electron transfer from the M−L complex to the nitro group.[3a]

Up to now, however, such an oxygen transfer to the C≡C group has not been reported. We now find intramolecular oxygen transfer from a nitro group to a C≡C bond for alkynes *o*-$NO_2C_6H_4$C≡CR (R = H or alkyls) mediated by an iridium hydride. Internal and terminal C≡C alkynes show different regiochemistry. For the terminal alkyne *o*-$NO_2C_6H_4$C≡CH O-transfer affords a product with an O*N*C_6H_4C(O)*C*H_2 group chelated via N and C, but for internal alkynes *o*-$NO_2C_6H_4$C≡CR (R = alkyl), we obtain a complex of the unusual heterocycle, anthranil.

2. Results and Discussion

2.1. Intramolecular Oxygen Transfer to Terminal Alkyne Groups. We recently reported the double insertion of a variety of electronically different alkynes into hydride **1** to afford η^2-butadienyl complexes (eq 1), including the insertion of alkyne *p*-$NO_2C_6H_4$C≡CH.[9] However, a dramatic change was observed when *o*-$NO_2C_6H_4$C≡CH was used instead.



Addition of 2 equiv of *o*-HC≡C(C_6H_4)NO_2 to a solution of **1** in CH_2Cl_2 at 0 °C affords an immediate color change from light yellow to black, from which a black precipitate **3** is isolated (65%) upon addition of ether (eq 2). Analytically pure **3** can be obtained by recrystallization using CH_2Cl_2 and Et_2O, if necessary. Product **3** is stable

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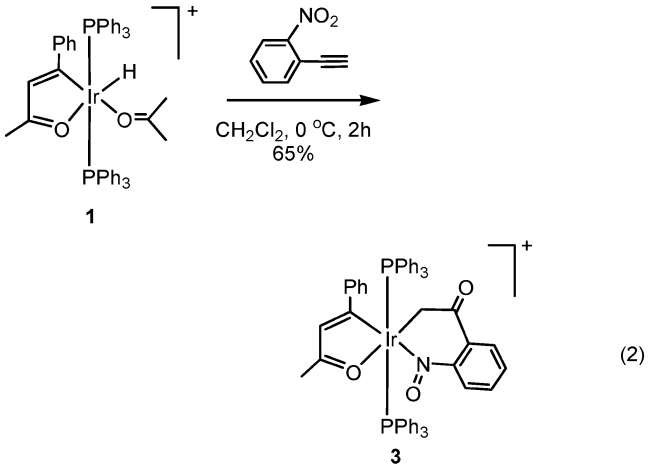
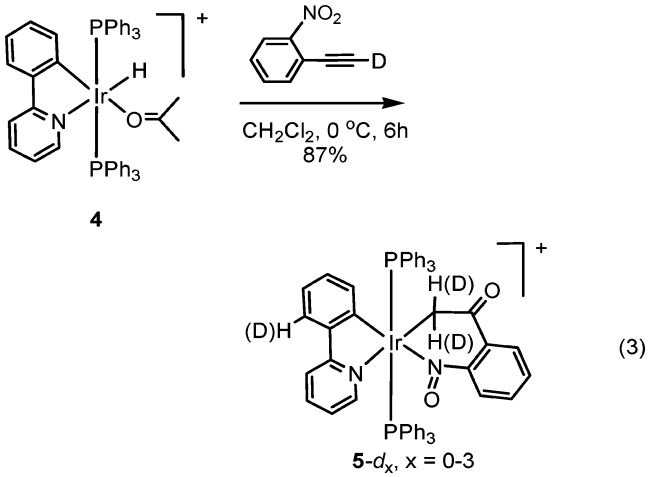
toward air and moisture in both solution or solid form. A similar yield was also obtained using acetone as a solvent.



(2)

The IR spectrum of **3** shows the presence of an organic CO (ν_{CO} = 1657 cm^{-1}) and an N-bound ArNO ligand (ν_{NO} = 1483 cm^{-1}).[8] Both ^{1}H and ^{13}C NMR spectroscopic data indicate the incorporation of only one alkyne unit, although excess *o*-HC≡C(C_6H_4)NO_2 is present. In the ^{1}H NMR spectrum (CD_2Cl_2) of **3**, the CH_2 group gives a characteristic triplet resonance at δ 3.85 (2H, $^3J_{PH}$ = 5.7 Hz), which becomes a singlet upon ^{31}P decoupling. In the ^{13}C{^{1}H} NMR spectrum (acetone-d_6), the *C*H_2 group gives a high-field resonance at δ 6.99 (t, $^2J_{PC}$ = 3.4 Hz). Similarly, *o*-HC≡C(C_6H_4)NO_2 also reacts with a related hydride **4** to yield a nitroso complex **5** (eq 3, shown for the deuterated alkyne), analogous to **3**. Comparable to **3**, the CH_2 protons resonate at δ 4.36 as a triplet ($^3J_{PC}$ = 4.1 Hz) in the ^{1}H NMR spectrum of complex **5** and the *C*H_2 resonates at δ 11.6 as a triplet ($^2J_{PC}$ = 4.4 Hz) in the ^{13}C{^{1}H} NMR spectrum. Both compounds **3** and **5** give a singlet signal in the ^{31}P{^{1}H} NMR spectra, indicating that the phosphines are trans.



(3)

Single crystals suitable for X-ray crystallography were obtained by slow diffusion of Et_2O into a dichloromethane solution of **3**. X-ray crystallography confirmed this as a rare iridium(III) alkyl nitroso complex. The crystal structure of **3** (Figure 1, Table 1) shows trans phosphine ligands. The Ir−C(1) bond (2.112(4) Å) is slightly longer than the Ir−C(12) bond (2.056(4) Å),

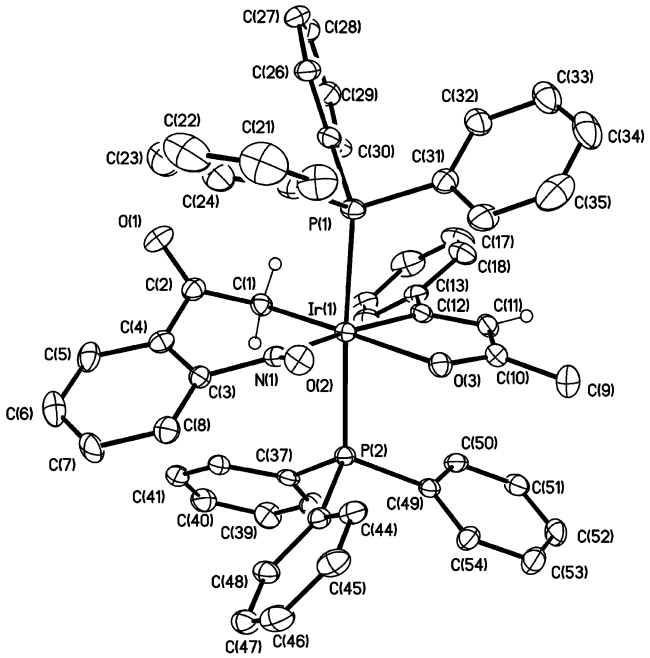


Figure 1. Molecular structure (ORTEP diagram) of the cation of **3** shown with 50% thermal ellipsoids. Hydrogen atoms are partially omitted for clarity.

Scheme 1. O-Transfer from Nitro to Oxidizable Groups

consistent with the alkyl nature of C(1). The phosphines are trans, with a P(1)−Ir(1)−P(2) angle of 174.56(4)°, consistent with the ^{31}P NMR data. The double-bond distance of N(1)−O(2) (1.231(5) Å) agrees with previous reports.[8a,10]

The differences between the reaction products from *o*-HC≡C(C_6H_4)NO_2 and *p*-HC≡C(C_6H_4)NO_2 suggests that the O-transfer is intramolecular. Further support comes from the reaction of complex **1** and PhC≡CH (2 equiv) in neat $PhNO_2$-d_5, which yields only butadienyl **2c**. All these observations support the intramolecularity of this O-transfer process.

The reaction of hydride **1** or **4** and *o*-HC≡C(C_6H_4)-NO_2 in acetone in the presence of 10 equiv of D_2O affords **3** or **5**, respectively, with no deuterium incorporation. This eliminates the possibility of the nitro group being reduced by H_2, generated from alkyne C−H oxidative addition to the iridium hydride, to give the nitroso and H_2O, followed by hydration of the Ir*C*≡*C* bond to form **3**. These results show that no OH group should be present.

Reflux (CH_2Cl_2, 2 days) of internal alkyne *o*-MeC≡C(C_6H_4)NO_2 and **4** returned only the starting materials. Therefore, alkyne C−H oxidative addition is probably necessary to form **5**. As shown in eq 3, a deuterium

(10) Little, R. G.; Deodens, R. J. *Inorg. Chem.* **1973**, *12*, 537.

Scheme 2. Possible Mechanisms of O-Transfer form Nitro to Oxidizable Groups

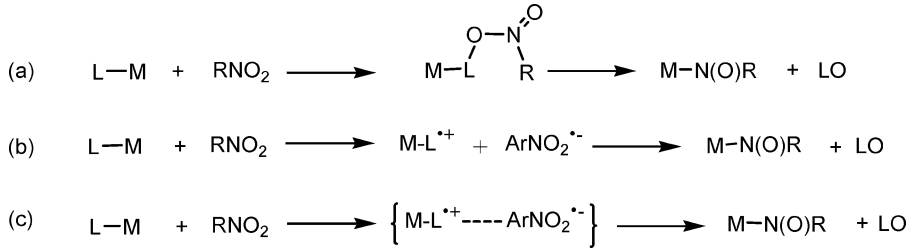


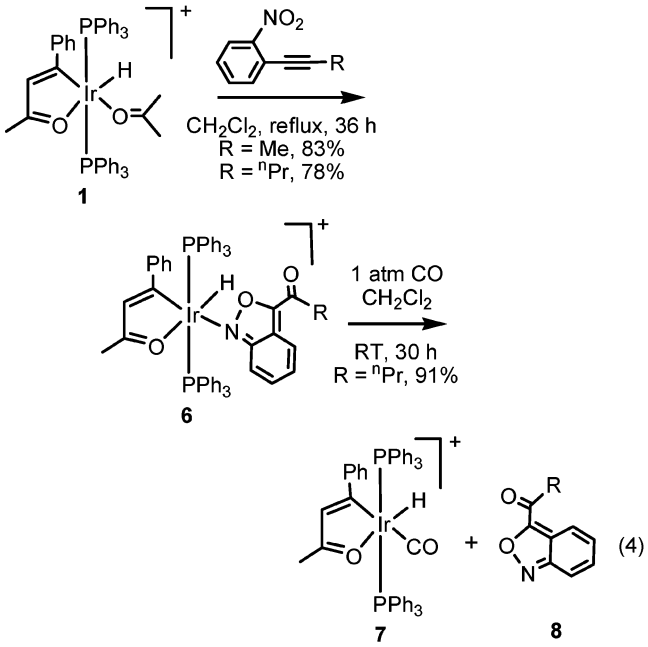
Table 1. Selected Bond Lengths and Angles for Complex 3

Bond Lengths (Å)	
Ir(1)−P(1)	2.389(1)
Ir(1)−P(2)	2.430(1)
Ir(1)−N(1)	2.046(4)
Ir(1)−C(1)	2.112(4)
Ir(1)−C(12)	2.056(4)
N(1)−O(2)	1.231(5)
Bond Angles (deg)	
P(1)−Ir(1)−P(2)	174.56(4)
Ir(1)−C(1)−C(2)	116.0(3)
Ir(1)−N(1)−O(2)	119.4(3)

labeling experiment using hydride **4** and 2 equiv of *o*-DC≡C(C_6H_4)NO_2 gives the product **5**-d_x (x = 0−3) as a mixture of four isotopomers based on the isotope pattern of the molecular ion peak in electrospray MS in a ratio of 26.5% for **5**-d_0, 43.1% for **5**-d_1, 22.2 for **5**-d_2, and 8.2 for **5**-d_3. Furthermore, both ^{1}H and ^{2}H NMR spectroscopy (CH_2Cl_2) confirmed the scrambling of deuterium to the CH_2 group (δ 4.36) and the 2-phenylpyridyl ligand (δ 7.08). The level of deuteration of the unreacted excess alkyne decreased from 99% in the starting alkyne to 82%.

A likely mechanism based on these results is shown in Scheme 3. The starting alkyne undergoes reversible C−H(D) oxidative addition through an Ir^{V}(H)(D) intermediate or an Ir^{III}(HD) complex,[11] consistent with the loss of deuterium in the unreacted alkyne.[9] The scrambling of the deuterium to the ligand arene ring is also expected from the Ir^{III}(HD) species (Scheme 3) on the basis of closely related reports via a C(aryl)−H agostic intermediate.[12] Intramolecular attack of the NO_2 oxygen on the Ir*C*≡C carbon of the alkynyl group yields an iridium vinyl hydride complex, which can then undergo a 1,2-hydride shift to generate the iridium alkyl, the carbonyl, and the nitroso groups.[2b] Chelation by the nitroso nitrogen finally leads to the deuterium scrambled product **5**.

2.2. O-Transfer to Internal Alkyne Groups. Unlike hydride **4**, hydride **1** reacts with internal alkynes RC≡C(C_6H_4)NO_2 (R = Me, ^{n}Pr) in refluxing CH_2Cl_2 to slowly afford another iridium hydride, **6** (eq 4). IR spectroscopy indicates the presence of an organic carbonyl group in **6** (R = Me, ^{n}Pr). The ^{1}H, ^{13}C, and ^{31}P-{^{1}H} NMR spectra of **6** (R = Me, ^{n}Pr) all showed fluxionality on the NMR time scale with slight broadening at 21 °C. When **6** (R = Me) was heated to 40 °C in CD_2Cl_2, further broadening was observed for each hydride and each methyl peak. Coalescence was not observed until the sample was heated to 80 °C in nitromethane-d_3. Electrospray MS (cation mode) also confirmed the presence of only one molecular ion for the seeming mixture of two components on the NMR time scale. Because of this complexity, elucidation of the structure of the product is difficult and X-ray crystallography seems the only efficient way, assuming only one rotamer can crystallize more easily than the other one.



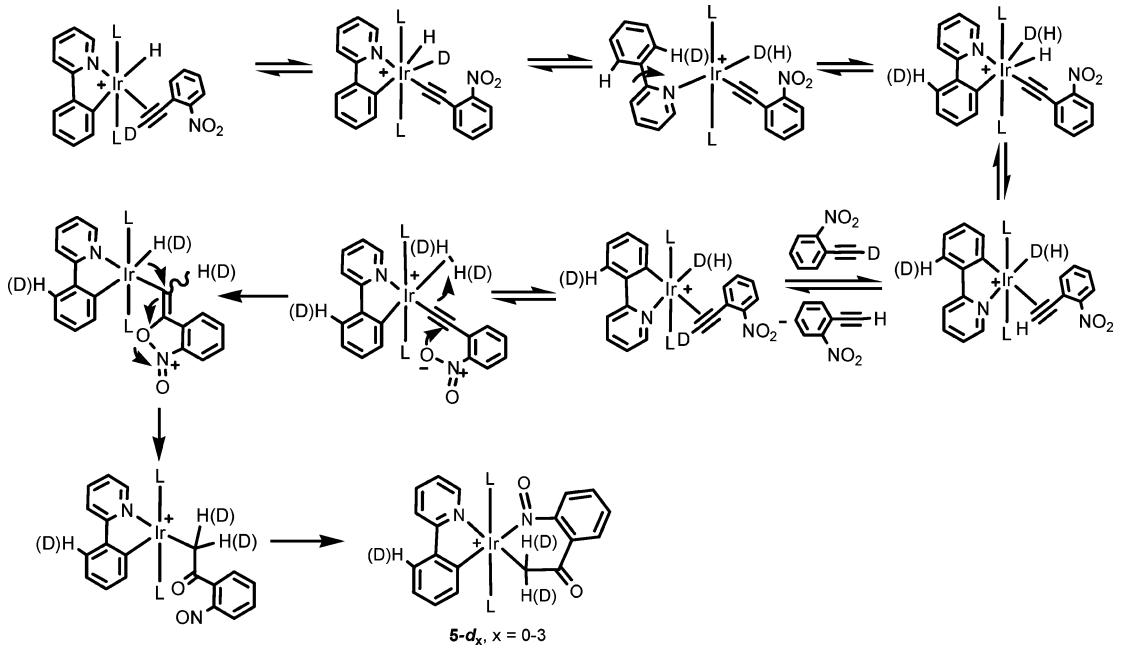
Fortunately, crystals of **6** (R = Me) suitable for X-ray analysis were obtained by slow diffusion of Et_2O into its CH_2Cl_2 solution. A crystallographic study of **6** (R = Me) revealed the octahedral geometry of the iridium complex and the presence of an unusual heterocycle, anthranil (**8**, R = Me), as a ligand coordinated at the nitrogen atom, trans to the vinyl C(4) (Figure 2, Table 2). The phosphines are in a trans arrangement with a P(1)−Ir(1)−P(2) angle of 172.23(4)°. The Ir(1)−N(1) bond distance is 2.095(4) Å. The electron density in the C−C anthranil backbone (C(11)−C(17)) is essentially delocalized, with C−C bond distances ranging from 1.376 to 1.424 Å. The C(18)−O(3) carbonyl group is in conjugation with the anthranil backbone. The hydride H(1) was located from the electron density difference map, with a fixed distance of 1.600(5) Å for ease of refinement.

Since the anthranil ligand coordinates to the iridium center though a dative Ir−N bond, we expect it to be substituted by CO. Indeed, stirring a solution of **6** (R =

(11) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 1, 242.

(12) (a) Toner, A.; Grundermann, S.; Clot, E.; Limbach, H.-H.; Donnadieu, B.; Sabo-Etienne, S. Chaudret, B. *J. Am. Chem. Soc.* **2000**, *122*, 6777. (b) Li, X.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 3378.

Scheme 3. Plausible Mechanism for the Formation of Nitroso Complex 5 from the Intramolecular O-Transfer



^{n}Pr) in CH_2Cl_2 under CO (1 atm) slowly yielded an iridium carbonyl complex **7** and free anthranil **8** (R = ^{n}Pr) (eq 4). The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy of the carbonyl complex was already known,[9b] and the identity of **8** (R = ^{n}Pr) was confirmed by comparison (^{1}H NMR spectrum) with **8** (R = ^{n}Pr) synthesized independently.[13]

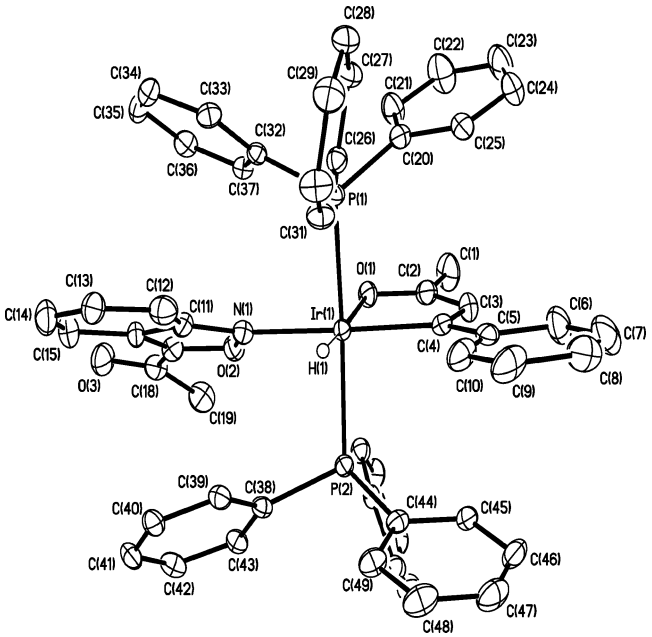


Figure 2. Molecular structure (ORTEP diagram) of the cation of **6** (R = Me) shown with 50% thermal ellipsoids. The hydride position is calculated.

Once the structure of **6** is clear and we know the difference between complexes **6** and starting material **1** is simply the substitution of the acetone ligand by an anthranil, an independent synthesis of **6** (R = ^{n}Pr) was conducted. **6** (R = ^{n}Pr) was synthesized in 95% yield as a yellow solid by refluxing **1** and 1 equiv of anthranil **8** (R = ^{n}Pr) in CH_2Cl_2. **6** (R = ^{n}Pr) synthesized in this method gives identical ^{1}H and ^{31}P{^{1}H} NMR spectra as that synthesized from **1** and *o*-^{n}PrC≡C(C_6H_4)NO_2 (eq 4).

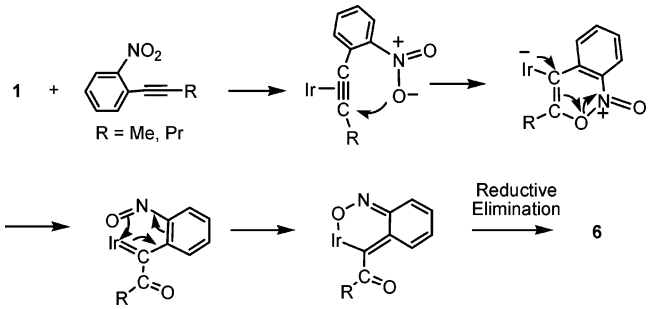
Table 2. Selected Bond Lengths and Angles for Complex 6 (R = Me)

Bond Lengths (Å)	
Ir(1)−P(1)	2.3425(14)
Ir(1)−P(2)	2.3467(14)
Ir(1)−N(1)	2.095(4)
Ir(1)−C(4)	2.027(5)
Ir(1)−H(1)	1.597(5)
Bond Angles (deg)	
P(1)−Ir(1)−P(2)	172.23(4)
C(4)−Ir(1)−O(2)	79.46(18)
Ir(1)−N(1)−C(11)	139.8(4)

The source of the fluxionality of the anthanil complexes was studied by VT NMR spectroscopy. Heating of a mixture of **6** (R = ^{n}Pr) and anthranil **8** (R = ^{n}Pr) in CD_2Cl_2 up to 40 °C shows no broadening of the free anthranil signals by ^{1}H NMR spectroscopy, while virtually every signal of the ^{1}H NMR spectra (CD_2Cl_2) of the pure **8** (R = ^{n}Pr) sample is slightly broadened at room temperature and significantly broadened at 40 °C. This is consistent with the fluxionality process being a hindered rotation about the Ir−N bond but inconsistent with any dissociation of the anthranil ligand. The linewidths of the anthranil methyl group in **6** (R = Me) were measured at various temperature (see Experimental Secton). A plot of ln(k/T) (where $k = \pi\Delta w_{1/2}$) against 1/T gives $\Delta H^{\ddagger} = 62.6$ kJ/mol and $\Delta S^{\ddagger} = -14$ J/(mol·K) with a $R^2 = 0.9998$. A small negative $\Delta S^{\ddagger}$ is most consistent with the more ordered transition state expected for a hindered bond rotation and not with any dissociation of the anthranil ligand. Models suggest that anthranil rotation must be accompanied by a correlated gearing motion of one PPh_3 group.

(13) Asao, N.; Sato, K.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 5675.

Scheme 4. Proposed Mechanism for the Formation of Iridium Anthranil Complexes



A plausible mechanism is proposed for the formation of **6** (Scheme 4). Nucleophilic attack of the nitro oxygen on the β-carbon of the alkyne ligand affords a carbene and a carbonyl ligand with the nitroso as a leaving group.[2b,14] This iridium carbene can then undergo a Cope-like cyclization to yield an iridium vinyl; finally C−O reductive elimination affords the iridium anthranil complex.[15]

The much greater reactivity of hydrides **1** over **4** toward internal alkynes MeC≡C(C_6H_4)NO_2 can probably be traced to their electronic difference. We previously showed that the iridium center in **4** is much more electron-rich than in **1**.[9b] Nucleophilic attack by the nitro oxygen will be disfavored when the coordinated alkyne in complex **4** attracts more back-donation. The reason for the difference of regiochemistry may be that the alkynyl complex is linear but the η^2-alkyne C≡C is bent so that the attacking O atom approaches the alkyne β-C more closely, making β-attack more favorable.

3. Conclusions

We have observed intramolecular O-transfer of the nitro group into C≡C bonds of *o*-RC≡C(C_6H_4)NO_2 mediated by iridium hydrides. For the terminal alkyne (R = H), rare iridium(III) nitroso complexes were isolated. For terminal alkynes (R = Me or ^{n}Pr), iridium hydride anthranil complexes were obtained as a result of O-transfer with a different regional chemistry. Mechanisms for these transformations, including a previously unknown O-transfer step from the nitro to the RC≡C bond, were proposed and crystal structures reported. A catalytic transformation of *o*-RC≡C(C_6H_4)NO_2 to the anthranil is currently under investigation.

4. Experimental Section

General Considerations. All the reactions were carried out under Ar, although all the products proved to be air stable. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 or Bruker 500 spectrometer. ^{31}P spectra were recorded on a Bruker 400 spectrometer with external standard (85% H_3PO_4). ^{2}H NMR spectra were recorded on a GE OMEGA 300 spectrometer with external CD_2Cl_2 standard. Elemental analyses were performed at the Atlantic Microlab. X-ray diffraction for single crystals was measured on a Nonius KappaCCD diffractometer.

Materials. Dichloromethane was distilled from CaH_2. Ether and pentane were used without further processing. Alkyne *o*-NO_2(C_6H_4)C≡CH was purchased from Aldrich. Deuterated alkyne *o*-NO_2(C_6H_4)C≡CD (99% D) was synthesized from base (NaOD)-catalyzed deuterium exchange with D_2O.[16] The synthesis of the iridium hydrides **1** and **4** was described before.[9]

Alkynes *o*-NO_2(C_6H_4)C≡CR (R = Me, ^{n}Pr) were synthesized from the Sonogashira coupling.[17] To a solution of *o*-NO_2(C_6H_4)I (2.50 g, 10 mmol) in NEt_3 (40 mL) at room temperature was added *cis*-$(PPh_3)_2PdCl_2$ (140 mg, 0.2 mmol). The resultant suspension was stirred for 10 min followed by addition of 1-pentyne (0.816 g, 12 mmol) and then CuI (20 mg, 0.1 mmol). This mixture was then stirred for 6 h, followed by removal of all volatiles under reduced pressure (ca. 0.5 mmHg). To this residue pentane was added twice (2 × 30 mL) followed by filtration and collection of the pentane solution. Flash column chromatography gave *o*-^{n}PrC≡C(C_6H_4)NO_2 (1.80 g, 9.5 mmol, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, 21 °C): δ 7.96 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.58 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.39 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 2.48 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 1.65 (sextet, $^3J_{HH}$ = 7.2 Hz, 2H), 1.07 (t, $^3J_{HH}$ = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.7 MHz, 21 °C): δ 150.5 (s), 135.2 (s), 132.9 (s), 128.3 (s), 124.8 (s), 119.8 (s), 99.7 (s, C≡C), 76.5 (s, C≡C), 22.3 (s), 22.2 (s), 13.9 (s). Analogously, *o*-NO_2-(C_6H_4)C≡CMe was synthesized from *o*-NO_2(C_6H_4)I and propyne gas in 93% yield.

Nitroso Complex 3(SbF_6^-). To a stirred CH_2Cl_2 solution (2 mL) of **1**(SbF_6^-) (200 mg, 0.173 mmol) was added a CH_2Cl_2 solution (2 mL) of *o*-NO_2(C_6H_4)C≡CH (51 mg, 0.347 mmol) at 0 °C. The solution immediately changed from light yellow to black and was then stirred for 2 h, warmed to room temperature, and concentrated to ca. 0.5 mL in vacuo. Et_2O (10 mL) was added to this solution to give a black powder, which was filtered, washed with Et_2O (15 mL), and dried in vacuo. Analytically pure **3**(SbF_6^-) was obtained by recrystallization using acetone/Et_2O. Yield: 140 mg (0.112 mmol, 65%). Dark red crystals of **3**(SbF_6^-) suitable for X-ray diffraction were obtained by slow diffusion of Et_2O to its CH_2Cl_2 solution after 1 day at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2, 294 K): δ 7.72 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.22−7.33 (m, 8H), 7.00−7.13 (m, 13H), 6.87−6.93 (m, 12H), 6.71 (d, $^3J_{H,H}$ = 7.8 Hz, 2H), 6.14 (s, 1H), 5.54 (d, $^3J_{H,H}$ = 8.3 Hz, 1H), 3.86 (t, $^3J_{PH}$ = 5.6 Hz, 2H, Ir−CH_2), 1.42 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 294 K): δ 213.6 (s, *C*=O), 205.6 (s, *C*=O), 202.1 (t, J_{PC} = 8.8 Hz, iridafuran Ir−*C*), 171.8 (s, C−N=O), 148.2 (s), 146.5 (s, CH), 139.5 (s), 138.3 (s), 135.5 (t, J_{PC} = 5.0 Hz, PPh_3), 133.3 (s), 132.8 (s, PPh_3), 131.2 (s), 130.0 (s), 129.9 (s), 129.5 (t, J_{PC} = 5.1 Hz, PPh_3), 128.9 (s), 125.1 (t, J_{PC} = 27.4, *ipso*-PPh_3), 118.4 (s), 26.1 (s, *C*H_3), 6.7 (t, J_{PC} = 3.6 Hz, Ir−CH_2). ^{31}P{^{1}H} NMR (161.9 MHz, acetone-d_6, 294 K): δ −4.04 (s). IR (CH_2Cl_2 film, cm^{-1}): 1657 (s, ν_{CO}), 1483 (s, ν_{NO}). Anal. Calcd for $C_{54}H_{45}F_6IrNO_3P_2Sb$: C, 52.05; H, 3.64; N, 1.12; F, 9.15. Found: C, 51.65; H, 3.64; N, 1.13; F, 9.10.

Nitroso Complex 5(BF_4^-). **5**(BF_4^-) was synthesized as a black powder in 87% yield by a method directly analogous to that for **3**(SbF_6^-) but starting from **4**(BF_4^-). Analytically pure **5**(BF_4^-) was obtained by recrystallization using CH_2Cl_2/Et_2O.

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^{1}H NMR (400 MHz, 294 K, CD_2Cl_2): δ 8.34 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 7.95 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.69 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.44 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.30 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.01−7.25 (m, 12H), 6.91 (t, $^3J_{HH}$ = 7.4 Hz, 12H, PPh_3), 6.67−6.72 (m, 12H, PPh_3), 6.54 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 4.36 (t, $^3J_{PH}$ = 4.1 Hz, 2H, Ir−CH_2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 294 K): δ 202.6 (t, J_{PC} = 4.4 Hz, C═O), 169.9 (s), 164.6 (s), 149.4 (s), 147.7 (s), 140.3 (s), 138.6 (s), 138.3 (s), 136.8 (s), 134.3 (t, J_{PC} = 4.8 Hz, PPh_3), 133.2 (s), 131.1 (s, PPh_3), 130.8 (t, J_{PC} = 10.0 Hz, Ir−C), 130.2 (s), 128.9 (s), 128.1 (t, J_{PC} = 4.8 Hz, PPh_3), 126.8 (t, J_{PC} = 26.8 Hz, *ipso*-PPh_3), 126.4 (s), 125.2 (s), 123.3 (s), 121.1 (s), 118.9 (s), 11.6 (t, J_{PC} = 4.4 Hz, Ir−CH_2). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 294 K): δ −11.17 (s). IR (cm^{-1}, CH_2Cl_2 film): 1655 (s, ν_{CO}), 1482 (s, ν_{NO}). Anal. Calcd for $C_{55}H_{44}BF_4IrN_2O_2P_2\cdot 0.5CH_2Cl_2$: C, 58.05; H, 3.95; N, 2.44; Cl, 3.09. Found: C, 58.22; H, 4.04; N, 2.43; Cl, 2.74.

Nitroso Complexes 5-*d*$_x$(BF_4^-) (*x* = 0−3). The synthesis of **5-*d*$_x$**(BF_4^-) (*x* = 0−3) was prepared as for **5**(BF_4^-) or **3**(SbF_6^-) starting from **4**(BF_4^-) (100 mg, 0.098 mmol) and *o*-NO_2-(C_6H_4)C≡CD (99% D, 29 mg, 0.196 mmol). The ^{1}H NMR spectrum (400 MHz, 294 K, CD_2Cl_2) of **5-*d*$_x$**(BF_4^-) (*x* = 0−3) is almost the same as that of **5**(BF_4^-) except that the signal at δ 4.36 becomes a multiplet (1.24 H). ^{2}H NMR (76.8 MHz, CH_2Cl_2, 294 K): δ 7.08 (s, 2-phenylpyridyl C_{phenyl}−D), 4.36 (s, Ir−CD). Electrospray MS [cation mode, mass (intensity)]: 1017.3 (20.4), 1018.4 (45.5), 1019.4 (75.2), 1020.4 (100), 1021.3 (81.3), 1022.3 (45.4), 1023.4 (16.1), and 1024.4 (3.9). This gives the following mixture: 26.5% **5-*d*$_0$,** 43.1% **5-*d*$_1$**, 22.2% **5-*d*$_2$**, and 8.2% **5-*d*$_3$**. The ether solution, from which complexes **5-*d*$_x$**-(BF_4^-) (*x* = 0−3) precipitate, was taken to dryness in vacuo and the unreacted alkyne recovered (21 mg, 85%). ^{1}H NMR analysis shows D% is 82% (18% H) for *o*-$NO_2C_6H_4C$≡C*H(D)*.

Anthranil Complex 6(SbF_6^-) (R = ^{n}Pr). Method 1. To a CH_2Cl_2 solution (6 mL) of **1**(SbF_6^-) (190 mg, 0.164 mmol) was added *o*-$NO_2(C_6H_4)$C≡C−^{n}Pr (46 mg, 0.244 mmol). The solution was then heated under reflux for 36 h, during which time the solution turned orange and then dark greenish yellow. The solvent was carefully concentrated to ca. 0.5 mL under reduced pressure, followed by precipitation with pentane (15 mL), to give a greenish yellow powder, which was filtered and washed with pentane (20 mL). Analytically pure **6**(SbF_6^-) (R = ^{n}Pr) was obtained as dark orange crystals by recrystallization using CH_2Cl_2/Et_2O. Yield: 165 mg (0.128 mmol, 78%). Method 2. To a CH_2Cl_2 (6 mL) solution of **1**(SbF_6^-) (150 mg, 0.130 mmol) was added anthranil **8** (R = ^{n}Pr).[4] The resultant solution was stirred for 3 h at 35 °C, followed by concentration of the solution to ca. 0.5 mL under reduced pressure. Addition of Et_2O (10 mL) afforded a yellow precipitate, which was filtered, washed with Et_2O (15 mL), and dried under vacuum. Yield: 159 mg (0.123 mmol, 95%). ^{1}H NMR (400 MHz, 295 K, CD_2Cl_2) shows there are two components (rotamers) in a ratio of 1 (minor):1.6 (major): δ 7.80 (d, $^3J_{HH}$ = 8.5 Hz, 2H minor, exchangeable with δ 7.51), 7.51 (d, $^3J_{HH}$ = 8.3 Hz, 2H major, exchangeable with δ 7.80), 6.98−7.49 (m), 6.72 (s, 1H, minor iridafuran CH, exchangeable with δ 6.19), 6.19 (s, 1H, major iridafuran CH, exchangeable with δ 6.72), 3.02 (br t, $^3J_{HH}$ = 6.9 Hz, 2H, minor C(O)CH_2, exchangeable with δ 2.82), 2.82 (t, $^3J_{HH}$ = 7.2 Hz, 2H, major C(O)CH_2, exchangeable with δ 3.02) 2.00 (s, 3H, major CH_3, exchangeable with δ 1.97), 1.97 (s, 3H, minor CH_3, exchangeable with δ 2.00), 1.88 (br m, 2H, minor C(O)$CH_2C\mathit{H}_2$, exchangeable with δ 1.72), 1.72 (sextet, $^3J_{HH}$ = 7.0 Hz, 2H, major C(O)$CH_2C\mathit{H}_2$, exchangeable with δ 1.88), 1.15(t, $^3J_{HH}$ = 6.8 Hz, minor CH_3, exchangeable with δ 1.02), 1.02 (t, $^3J_{HH}$ = 7.2 Hz, minor CH_3, exchangeable with δ 1.15), −20.60 (t, $^2J_{PH}$ = 13.4 Hz, 1H, minor Ir−H, exchangeable with δ −20.62), −20.62 (t, $^2J_{PH}$ = 13.7 Hz, 1H, major Ir−H, exchangeable with δ −20.60). ^{13}C{^{1}H} NMR (125.8 MHz, CD_3NO_2, 294 K): δ 213.9 (s, major iridafuran C═O, exchangeable with δ 213.4), 213.4 (s, minor iridafuran C═O, exchangeable with δ 213.9), 201.5 (t, J_{PC} = 6.8 Hz, major Ir−C, exchangeable with δ 209.2), 209.2 (t, J_{PC} = 6.9 Hz, minor Ir−C, exchangeable with δ 210.5), 190.3 (s, minor C═O, exchangeable with δ 190.2), 190.2 (s, major C═O, exchangeable with δ 190.3), 160.6 (s, major C, exchangeable with δ 160.3), 160.3 (s, minor C, exchangeable with δ 160.6), 159.2 (s, major C, exchangeable with δ 157.6), 157.6 (s, minor C, exchangeable with δ 159.2), 148.8 (s, major C, exchangeable with δ 145.5), 145.5 (s, minor C, exchangeable with δ 148.8), 135.7 (t, J_{PC} = 5.3 Hz, minor PPh_3, exchangeable with δ 135.3), 135.6 (s, CH), 135.3 (t, J_{PC} = 5.0 Hz, major PPh_3, exchangeable with δ 135.7), 135.1 (s, minor CH, exchangeable with δ 134.9), 134.9 (s, major CH, exchangeable with δ 135.1), 132.7 (s, minor CH, exchangeable with δ 131.2), 132.2 (s, *para*-PPh_3), 132.1 (s, minor CH, exchangeable with δ 131.8), 131.8 (s, major CH, exchangeable with δ 132.1), 131.2 (s, major CH, exchangeable with δ 132.7), 131.02 (s, minor CH, exchangeable with δ 130.98), 129.6 (t, J_{PC} = 5.0 Hz, major PPh3, exchangeable with δ 129.4), 129.5 (t, J_{PC} = 27.3 Hz, major *ipso*-PPh_3, exchangeable with δ 129.1), 129.2 (s, CH), 129.1 (t, J_{PC} = 27.3, minor *ipso*-PPh_3, exchangeable with δ 129.5), 122.5 (s, minor CH, exchangeable with δ 122.4), 122.4 (s, major CH, exchangeable with δ 122.5), 121.6 (s, major C, exchangeable with δ 121.3), 121.3 (s, minor C, exchangeable with δ 121.6), 118.0 (s, minor C, exchangeable with δ 117.6), 43.9 (s, minor C(O)$C\mathit{H}_2$, exchangeable with δ 43.5), 43.5 (s, major C(O)$C\mathit{H}_2$, exchangeable with δ 43.9), 26.5 (s, major CH_3, exchangeable with δ 26.4), 26.4 (s, minor CH_3, exchangeable with δ 26.5), 18.2 (s, minor C(O)$CH_2C\mathit{H}_2$, exchangeable with δ 17.9), 17.9 (s, major C(O)$CH_2C\mathit{H}_2$, exchangeable with δ 18.2), 14.5 (s, minor C(O)$CH_2CH_2C\mathit{H}_3$, exchangeable with δ 14.3), 14.3 (s, major C(O)$CH_2CH_2C\mathit{H}_3$, exchangeable with δ 14.5). ^{13}C{^{1}H} NMR (125.8 MHz, CD_3NO_2, 358 K): δ 214.0 (s, iridafuran C═O), 210.0 (br s, Ir−C), 190.2 (s, anthranil C═O), 161.2 (s, anthranil C), 158.8 (br s, anthranil C), 135.7 (br s, PPh_3), 135.6 (s, CH), 135.3 (s, CH), 132.5 (s, *para*-PPh_3), 132.3 (br s, CH), 132.2 (s, CH), 131.1 (s, CH), 130.0 (t, J_{PC} = 27.5, *ipso*-PPh_3) 129.7 (br t, J_{PC} = 4.8 Hz, PPh_3,), 129.6 (s, CH), 122.8 (s, anthranil CH), 121.9 (s, anthranil C), 118.0 (s, anthranil CH), 44.0 (s, C(O)$C\mathit{H}_2$), 26.6 (s, CH_3), 18.4 (s, C(O)$CH_2C\mathit{H}_2$), 14.5 (s, r C(O)$CH_2CH_2C\mathit{H}_3$). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 294 K): 15.76 (s, minor), 15.51 (s, major). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 358 K): 15.88 (s). IR (CH_2Cl_2 film, cm^{-1}): 1690 (s, ν_{CO}), 2240 (br, ν_{Ir-H}). Electrospray MS for $C_{57}H_{51}NO_3IrP_2^+$ [mass (intensity)]: 1050.5 (53.3), 1051.5 (33.3), 1052.5 (100), 1053.5 (58.7), 1054.5 (18.1), 1055.5 (3.9). Calcd mass (intensity): 1050.3 (53.2), 1051.3 (33.3), 1052.3 (100), 1053.3 (58.3), 1054.3 (18.1), 1055.3 (3.7). Anal. Calcd for $C_{57}H_{51}F_6IrNO_3P_2$: C, 53.16; H, 3.99; N, 1.09. Found: C, 53.39; H, 4.07; N, 1.07.

Table 3. VT NMR Measurement of the Fluxionality of Complex 6 (R = Me)

T (K)	1000 × 1/*T* (1/K)	$\Delta(W_{1/2})$ (Hz)	*k* (Hz)	ln(*k*/*T*)
283.1	3.534	0.99	3.11	−4.511
289.1	3.460	1.72	5.40	−3.980
295.1	3.389	2.94	9.24	−3.463
300.1	3.333	4.56	14.32	−3.042
305.1	3.279	7.19	22.60	−2.602
310.1	3.226	10.92	34.31	−2.201
315.1	3.175	16.17	50.77	−1.824

Reaction of Anthranil Complex 6(SbF_6^-) (R = ^{n}Pr) and CO. A CH_2Cl_2 solution (6 mL) of **6**(SbF_6^-) (R = ^{n}Pr, 200 mg, 0.155 mmol) was stirred under CO (l atm) for 30 h at 25 °C. The resultant greenish yellow solution was concentrated to ca. 0.2 mL, followed by addition of Et_2O (20 mL), to give a greenish yellow precipitate **7**(SbF_6^-). Yield: 159 mg (0.141 mmol, 91%). ^{1}H NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 7.55 (t, $^3J_{HH}$ = 7.1 Hz, 6H, P*Ph*$_3$), 7.37−7.47 (m, 24H), 7.25−7.29 (m, 3H), 7.08 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 6.79 (s, 1H, iridafuran C*H*), 1.90 (s, 3H, C*H*$_3$), −18.90 (t, $^2J_{PH}$ = 11.7 Hz, Ir−H). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 5.83 (s). IR (CH_2Cl_2 film): 2042 cm^{-1} (ν_{CO}). Comparison of these data with previous literature confirmed the identity of this complex.[2b] The ether

Table 4. Crystallographic Data for 3 and 6 (R = Me)

	3·CH_2Cl_2	**6**·0.5CH_2Cl_2 (R = Me)
empirical formula	$C_{56}H_{49}Cl_4F_6IrNO_3P_2Sb$	$C_{55.5}H_{48}ClF_6IrNO_3P_2Sb$
molecular weight (g mol^{-1})	1415.65	1302.29
radiation, λ (Å)	Mo Kα (monochr), 0.71073 Å	
T (°C)	−100	−100
cryst syst	monoclinic	monoclinic
space group	$P1$ (#2)	$P1$ (#2)
a (Å)	13.542(3)	11.151(2)
b (Å)	13.872(3)	11.747(2)
c (Å)	14.801(3)	20.581(4)
α (deg)	102.95(3)	84.86(3)
β (deg)	90.03(3)	86.68(3)
γ (deg)	94.13(3)	72.19(3)
V (Å^3)	2702.1(9)	2554.9(9)
Z	2	2
D_{calcd} (g cm^{-3})	1.740	1.693
μ(Mo Kα) (cm^{-1})	32.83	33.12
cryst size (mm)	0.25 × 0.10 × 0.08	0.15 × 0.10 × 0.10
total, unique no. of rflns	20 440, 11 729	17 945, 10 033
R_{int}	0.0336	0.0393
no. of observations used	11 729	10 033
no. of params, restrictions	614, 0	654, 1
R^a, $R_w{}^b$	0.0391; 0.092	0.0359; 0.0684
GOF	1.035	1.055
min., max. resid dens (e Å^{-3})	−1.279, 1.112	−1.092, 0.961

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 2\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

solution, from which complex **7**(SbF_6^-) precipitates, was taken to dryness in vacuo, followed by addition of pentane (15 mL) and filtration. The pentane solution was collected, and removal of pentane gives **8** (R = ^{n}Pr). Yield: 26.4 mg (0.140 mmol, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 8.05 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 7.40 (ddd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 6.5 Hz, $^5J_{HH}$ = 1.1 Hz, 1H), 7.27 (ddd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 6.5 Hz, $^5J_{HH}$ = 1.0 Hz, 1H), 3.14 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C(O)CH_2CH$_2$CH$_3$), 1.83 (sextet, $^3J_{HH}$ = 7.3 Hz, 2H, CH$_2$CH_2-CH$_3$), 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 295 K): 190.5 (s, C), 160.3 (s, C), 158.0 (s, C), 131.6 (CH), 128.8 (CH), 121.5 (s, CH), 119.3 (s, C), 116.2 (s, CH), 42.4 (s, CH_2), 17.4 (s, CH_2), 13.9 (s, CH_3). IR (CH_2Cl_2 film, cm^{-1}): 1689 (s, ν_{CO}). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.62; H, 5.93; N, 7.28. An independent synthesis of anthranil **8** (R = ^{n}Pr) confirmed its identity.[4]

Anthranil Complex 6(SbF_6^-) (R = Me). To a CH_2Cl_2 solution (6 mL) of **1**(SbF_6^-) (190 mg, 0.164 mmol) was added *o*-$NO_2(C_6H_4)$C≡CMe (40 mg, 0.248 mmol). The solution was then heated under reflux for 36 h, during which time the solution turned orange and then dark greenish brown. The solvent was carefully concentrated to ca. 0.5 mL under reduced pressure, followed by precipitation with pentane (10 mL), to give a greenish yellow powder, which was filtered and washed with pentane (20 mL). Analytically pure **6**(SbF_6^-) (R = Me) was obtained as dark orange crystals by slow diffusion of Et_2O into a solution of CH_2Cl_2 after 1 day, which is also suitable for X-ray crystallographic analysis. Yield: 170 mg (0.135 mmol, 82%). ^{1}H NMR (400 MHz, 294 K, CD_2Cl_2) shows there are two components (rotamers) in 1 (minor):1.5 (major) ratio: δ 7.77 (d, $^3J_{HH}$ = 7.2 Hz, 2H, minor), 7.49 (d, $^3J_{HH}$ = 7.0 Hz, 2H, major), 6.98−7.46 (m), 6.71 (s, 1H, minor, iridafuran CH), 6.14 (s, 1H, major, iridafuran CH), 2.73 (s, 3H, minor, CH_3), 2.53 (s, 3H, major, CH_3), 1.98 (s, 3H, major, CH_3), 1.96 (s, 3H, minor, CH_3), −20.60 (t, $^2J_{PH}$ = 13.2 Hz, 1H, minor Ir−H), −20.61 (t, $^2J_{PH}$ = 13.7 Hz, 1H, major Ir−H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_3NO_2, 358 K): δ 213.9 (s, iridafuran C=O), 210.0 (br s, Ir−C), 187.4 (s, anthranil C=O), 161.2 (s, C), 158.8 (br s, C), 135.8 (s), 135.7 (br s, PPh_3), 135.3 (s, CH), 132.5 (s, *para*-PPh_3), 132.3 (br s, CH), 132.2 (s, CH), 131.2 (s, CH), 130.0 (t, J_{PC} = 27.3, *ipso*-PPh_3) 129.7 (br t, J_{PC} = 4.8 Hz, PPh_3,), 129.6 (s, CH), 122.6 (s, CH), 121.9 (s, C), 118.1 (s, CH), 28.6 (s, CH_3), 26.5 (s, CH_3). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 294 K): 15.99 (s, minor), 15.72 (s, major). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 358 K): 15.80 (s). IR (CH_2Cl_2 film, cm^{-1}): 1692 (s, ν_{CO}), 2241 (br, ν_{Ir-H}). Electrospray MS for $C_{55}H_{47}NO_3IrP_2^+$[mass (intensity)]: 1022.3 (53.8), 1023.3 (32.8), 1024.3 (100), 1025.3 (60.4), 1026.3 (18.6), 1027.3 (3.5). Calcd mass (intensity): 1022.3 (53.6), 1023.3 (32.5), 1024.3 (100), 1025.3 (59.6), 1026.3 (18.1), 1027.3 (3.3). Anal. Calcd for $C_{55}H_{47}F_6IrNO_3P_2$·0.5CH_2Cl_2: C, 51.18; H, 3.71; N, 1.08. Found: C, 51.56; H, 3.74; N, 1.26. The stoichiometry of the CH_2Cl_2 was confirmed by X-ray crystallography.

VT NMR Measurement of Anthranil Complex 6(SbF_6^-) (R = Me). VT NMR spectra (500.1 MHz) were recorded for a CD_2Cl_2 solution (0.6 mL) of **6**(SbF_6^-) (R = Me, 28 mg) at T = 248.1, 283.1, 289.1, 295.1, 300.1, 305.1, 310.1, and 315.1 K. The resonance at δ 2.53 was analyzed to give half-peak width broadening ($\Delta w_{1/2}$) of 1.68, 2.67, 3.40, 4.62, 6.24, 8.87, 12.60, and 17.85 Hz, respectively (Table 3). A plot of ln(k/T) (where $k = \pi\Delta w_{1/2}$) against 1/T gives $\Delta H^‡$ = 62.6 kJ/mol and $\Delta S^‡$ = −14 J/(mol·K) with a R^2 = 0.9998.

5. Crystallography

Structure Determination of Complexes 3 and 6 (R = Me). Crystals of **3** or **6** (R = Me) were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **3** over 1 day. Suitable crystals were selected and mounted on thin glass fibers using epoxy cement and cooled to data collection temperature. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation, and intensity data were collected by using the ω-scan mode. The data were corrected for Lorentz and polarization effects, and no absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions.

Complex **3** cocrystallized with dichloromethane in a ratio of 1:2 (**3**·2CH_2Cl_2). The space group for this crystal is triclinic $P\bar{1}$ with one molecule in the asymmetric unit and two molecules in the unit cell. The SbF_6^- anion is plagued with unresolved positional disorder, and although the antimony and fluorine were refined anisotropically, one residue peak remains on the electon difference map in very close proximity to the anion, and fluorine atoms possess inflated thermal parameters. Squeeze/Platon[18] was applied to resolve the severely disordered

(18) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

two dichoromethane molecules within the asymmetric unit. Within the 456.2 Å^3 unit cell void space occupied by solvent molecules, a total of 164 electrons were calculated, compared to 168 electrons for the four molecules of solvent. In this treatment of solvent, the contributions of the solvent molecules are collective and not as individual atoms. Hence, the atom list does not contain the atoms of the solvent molecules.

Complex **6** (R = Me) cocrystallized with dichloromethane in a ratio of 2:1 (**6**·0.5CH_2Cl_2). The space group for this crystal is triclinic $P\bar{1}$ with one molecule in the asymmetric unit and two molecules in the unit cell. The half-molecule of CH_2Cl_2 resides on a crystallographic inversion center and possesses symmetry-imposed disorder. The hydride H(1) was located from the electron difference map, but the Ir(1)−H(1) bond was restrained to a distance of 1.600(5) Å for ease of refinement. This distance is comparable to several related structures in the Cambridge Crystallographic Database (v.5.25, July 2004). Crystallographic data for complexes **3** and **6** (R = Me) are displayed in Table 4.

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Supporting Information Available: Detailed X-ray crystallographic data (atomic positional parameters, bond distances, bond angles, and anisotropic parameters) for complexes **3** and **6** (R = Me) in PDF and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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