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Cationic Complexes of Iridium: Diiodobenzene Chelation, Electrophilic Behavior with Olefins, and Fluxionality of an Ir(I) Ethylene Complex

Paul J. Albietz, Jr., Brian P. Cleary, Witold Paw, and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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The synthesis of a series of dicationic Ir(III) complexes is described. Reaction of Ir(CO)(dppe)I (dppe = 1,2-bis(diphenylphosphino)ethane)) with RI (R = CH_3 and CF_3) results in formation of the Ir(III) precursors IrR(CO)(dppe)$(I)_2$ (R = CH_3 (**1a**) and CF_3 (**1b**)). Subsequent treatment with AgOTf (OTf = triflate) generates the bis(triflate) analogues IrR(CO)(dppe)$(OTf)_2$ (R = CH_3 (**2a**) and CF_3 (**2b**)), which undergo clean metathesis with NaBARF (BARF = $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$) in the presence of 1,2-diiodobenzene (DIB) forming the dicationic halocarbon adducts [IrR(CO)(dppe)(DIB)]$[BARF]_2$ (R = CH_3 (**3a**) and CF_3 (**3b**)). Complexes **3a** and **3b** demonstrate facile exchange chemistry with acetonitrile and carbon monoxide forming complexes **4** and **5**, respectively. NMR investigation of the mechanism reveals that the process proceeds through an η^1-diiodobenzene adduct, where labilization at the coordination site trans to the alkyl group occurs first. Complex **3a** reacts with ethylene forming the cationic iridium(I) product $[Ir(C_2H_4)_2(CO)(dppe)][BARF]$ (**6**), which demonstrates fluxional behavior. Variable-temperature NMR studies indicate that the five-coordinate complex **6** undergoes three dynamic processes corresponding to ethylene rotation, Berry pseudorotation, and intermolecular ethylene exchange in order of increasing temperature based on NMR line shape analyses used to determine the thermodynamic parameters for the processes. The DIB adducts **3a** and **3b** were also found to promote olefin isomerization of 1-pentene, and polymerization/oligomerization of styrene, α-methylstyrene, norbornene, β-pinene, and isobutylene via cationic initiation.

Introduction

The design and synthesis of “electrophilic” late transition metal complexes for conducting bond activation chemistry is an area of growing interest in organometallic chemistry and catalysis. One of the earliest examples of a late metal complex capable of promoting electrophilically driven transformations is the palladium(II) species $[Pd(NCMe)_4][BF_4]_2$, which, owing to the lability of its ligands and the 2+ charge for C=C bond polarization and activation, was found to (1) polymerize styrene,[1] ethyl vinyl ether,[2] *N*-vinylcarbazole,[2] and 1,3-cyclohexadiene;[3] (2) oligomerize ethylene into C_4, C_6, C_8, and C_{10} products;[1] (3) isomerize 1-butene[1] into *trans*- and *cis*-2-butene; and (4) promote other organic transformations.[2,4,5] Sen and co-workers also described other electrophilic solvento complexes to promote related transformations.[2,6,7]

The activation and functionalization of C−H bonds of organic molecules using cationic late metal centers is also an area of research that has gained considerable attention. Due to the natural abundance of hydrocarbons, facile conversion into more useful materials is a goal that is avidly being pursued by chemists in both academia and industry. Some recent examples[8−10] of C−H bond activation of hydrocarbons describe use of $[(Cp^*)IrMe(PMe_3)(CH_2Cl_2)]^+$ and $[PtMe(sol)(NN)]^+$ complexes (NN = Me_4en or Ar_2DAB, sol = weakly coordinating solvent) where bond cleavage is observed under relatively mild reaction conditions. In these systems, the common thread is generation of a cationic metal−alkyl complex where weakly coordinating solvents/ligands and noncoordinating counterions are used to avoid deactivation of the metal center.

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* Author to whom correspondence should be addressed. E-mail: rse7@chem.rochester.edu.

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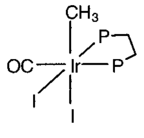
Perhaps one of the most impressive examples[11-16] employing an electrophilic late metal system is that using the cationic diimine complex $[Pd(Me)(sol)(Ar_2DAB)]^+$ (Ar_2DAB = diaryldiazabutadiene, sol = coordinated solvent) for ethylene and α-olefin polymerizations. The reported palladium(II) complexes demonstrate catalytic activities comparable to those of the extensively studied metallocenes,[11,17,18] and allow for alteration of the polymer characteristics by changing the substituents on the aryl ring of the Ar_2DAB. Similar success has also been achieved for CO/C_2H_4 copolymerizations using the related palladium(II) systems[19] $[PdMe(sol)(L\text{-}L)]^+$ (L-L = diimine or diphosphine and sol = coordinated solvent).

As a d^6 metal ion, Ir(III) is thought to possess electrophilic character similar to that of Pd^{2+} but its configuration in a coordinatively saturated environment confers inertness on its cationic complexes. In the study noted above involving $[(Cp^*)IrMe(PMe_3)(CH_2Cl_2)]^+$, Bergman showed that this inertness can be overcome through the use of a halocarbon as a weakly coordinating ligand.[8] Specifically, in the presence of $^{13}CH_4$, exchange of the methyl ligand is seen which proceeds by dichloromethane loss and C−H bond activation. Similarly, past work by Crabtree[20] has shown that reaction of $C_6H_4I_2$ with the labile Ir(III) disolvate $IrH_2(Me_2CO)_2(PPh_3)_2^+$ results in clean coordination of the halocarbon forming $IrH_2(C_6H_4I_2)(PPh_3)_2^+$. Complete structural characterization of the adduct was accomplished, including an X-ray diffraction analysis.

In studies designed to generate Ir(III) complexes having adjacent labile sites, the syntheses of the bis(triflate) complex $IrCH_3(CO)(dppe)(OTf)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane, OTf = triflate) and the dicationic acetyl complex $[Ir(C(O)CH_3)(dppe)(MeCN)_3]^{2+}$ were previously reported.[21] The triflate complex was shown to be a weak electrolyte in dichloromethane, and the acetonitrile complex gave evidence of moderately facile exchange in the position trans to the Me ligand. In continuing efforts focused on exploring the electrophilic behavior of these iridium(III) systems, we recently described the generation of two adducts of 1,2-diiodobenzene (DIB) following Crabtree's approach[20] and found the resultant complexes to exhibit electrophilic behavior leading to polymerization or oligomerization of several olefins.[22] Herein we report in detail the synthesis and characterization of these DIB complexes along with their observed reaction chemistry with different olefinic substrates. The study also describes the synthesis of a bis(ethylene) complex of Ir(I) obtained in this investigation and its fluxional behavior.

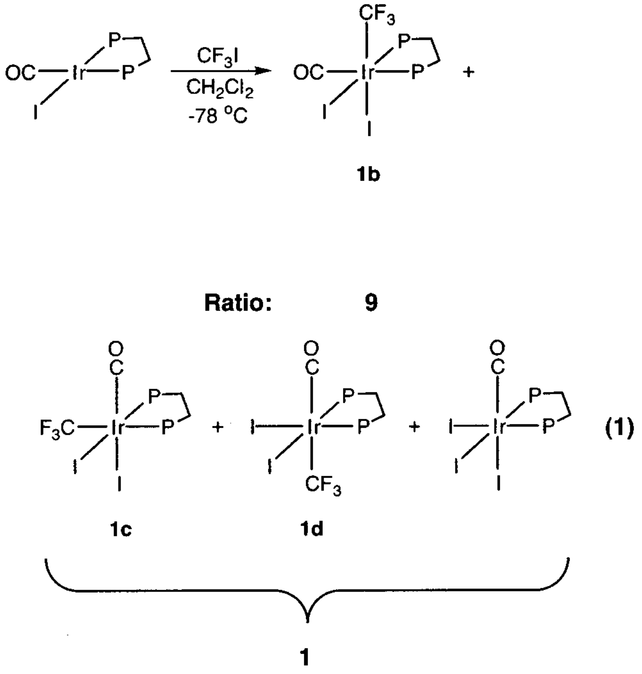
Results and Discussion

Synthesis of $IrR(CO)(dppe)I_2$ Where R = CH_3 and CF_3 (1a and 1b). The synthesis of the Ir(III) precursor complexes may be accomplished by conducting an oxidative addition reaction in CH_2Cl_2 between Ir(dppe)(CO)I and either CH_3I at room temperature or CF_3I at −78 °C. Complete structural data (NMR, micro, and X-ray analyses) for complex **1a** have been previously described.[23] The geometry of **1a** was assigned on the basis of observation of two ^{31}P resonances at δ 23.9 and −3.61 (J_{P-P} = 4.9 Hz) for dppe, the methyl ^1H resonance at 0.56 ppm as a doublet of doublets (J_{H-P} = 4.1 and 6.7 Hz), and the coupling of the carbonyl ^{13}C resonance (δ = 169.7) showing that it is trans to one dppe donor (and cis to the other with J_{C-P} of 146 and 6 Hz).



1a

Synthesis of the corresponding trifluoromethyl complex **1b** was undertaken to generate a complex having enhanced electrophilicity at the Ir(III) center relative to **1a** and without an alkyl ligand capable of migratory insertion, as had been seen for **1a**.[21] Reaction of CF_3I with the Ir(I) precursor Ir(dppe)(CO)I at room temperature produces three geometric isomers [**1b**:**1c**:**1d** (ratio = 1:4:1)] of $IrCF_3(CO)(dppe)I_2$, in addition to minor amounts of the triiodide complex *fac*-Ir(CO)(dppe)I_3.[24] However, when the oxidative addition is conducted at −78 °C, approximately 90% formation of isomer **1b** (eq 1) results. After chromatographic purification, this isomer can be obtained as a yellow air-stable solid in 80% yield.



Orientation of the CF_3 group relative to dppe may be unambiguously determined on the basis of the J_{F-P} coupling

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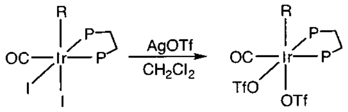
constants, where $J_{\mathrm{F-P}}(\mathrm{cis}) \approx 4-10$ Hz and $J_{\mathrm{F-P}}(\mathrm{trans}) \approx 40-50$ Hz. (See Supporting Information Figure S.9.) Moreover, the asymmetry of complex **1b** and the magnitudes[25] of the $J_{\mathrm{C-P}}$ coupling constants (5.7 and 139.7 Hz) indicate that the CO ligand has both trans and cis orientations relative to dppe phosphine donors, thereby substantiating the assignment. With regard to IR characterization of the compound, the ν_{CO} of **1b** is 28 cm^{-1} higher in energy than the methyl analogue **1a**, demonstrating the electron-withdrawing effect of the CF_3 group. In all of the complexes described in this paper, the ~25−30 cm^{-1} difference in ν_{CO} between the CH_3 and CF_3 analogues is a general trend.

Synthesis of IrR(CO)(dppe)(OTf)$_2$ Where R = CH$_3$ and CF$_3$ (2a and 2b). Halide abstraction from the diiodide complex **1b** using AgOTf in CH_2Cl_2 (eq 2) proceeds cleanly, forming IrCF$_3$(CO)(dppe)(OTf)$_2$ (**2b**) in 70% yield, similar to that reported for **1a**.[21] Complex **2b** is a white solid that demonstrates limited solubility in CH_2Cl_2. The product retains the geometry of the starting complex as indicated by small $J_{\mathrm{F-P}}$ values (≈6 Hz) for phosphorus coupling to the CF_3 group and the $J_{\mathrm{C-P}}$ values (130 and 6.1 Hz) for coupling between the CO ligand and dppe phosphine donors. In the ^{19}F NMR spectrum of the complex, three resonances of equal intensity are observed, one at δ 55.88 for the Ir−CF$_3$ group and the other two located further upfield at δ −13.62 and −14.30 for the inequivalent OTf$^-$ ligands.

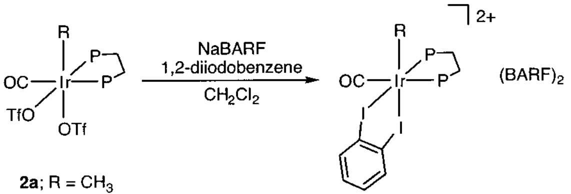


(2)

1a; R = CH$_3$
1b; R = CF$_3$

2a; R = CH$_3$
2b; R = CF$_3$

Synthesis of [IrR(CO)(dppe)(*o*-diiodobenzene)][BARF]$_2$ Where R = CH$_3$ and CF$_3$ (3a and 3b). Synthesis of diiodobenzene adducts **3a** and **3b** (eq 3) can be accomplished starting from the Ir(III) bis(triflate) complexes IrR(CO)(dppe)(OTf)$_2$, **2**. When metathesis of the coordinated OTf$^-$ ligands of either **2a** or **2b** is carried out with 3 equiv of NaBARF in CH_2Cl_2 in the presence of 3 equiv of diiodobenzene, formation of a single iridium species is observed. After filtration of the NaOTf precipitate and subsequent solvent evaporation, thermally stable off-white solids are obtained in high yields (80−90%). The diiodobenzene adducts are very soluble in CH_2Cl_2, slightly less soluble in Et_2O, insoluble in hydrocarbon solvents (benzene, toluene, hexane, etc.), and reactive with more polar solvents (MeCN, acetone, alcohols, $MeNO_2$, etc.). As described below, some of the reactions result in clean displacement of diiodobenzene to generate the Ir(III) disolvento species. Polymerization of THF by these complexes also occurs and supports their presumed electrophilic nature.



(3)

2a; R = CH$_3$
2b; R = CF$_3$

3a; R = CH$_3$
3b; R = CF$_3$

Complexes **3a** and **3b** demonstrate clean spectroscopic features in their ^{31}P, ^{19}F, and ^{1}H NMR spectra. Complete metathesis of the OTf$^-$ ions is evidenced by the absence of the triflate resonances in the ^{19}F NMR spectrum, and by the presence of aryl CF_3 groups of the BARF anion at 0.24 ppm. Likewise, 1:1 resonances in the ^{31}P{^{1}H} NMR spectra (δ 27.28 and 3.95 for **3a**; δ 25.74 and −1.20 for **3b**) indicate that the complexes each have two inequivalent ^{31}P environments resulting from different ligands trans to the dppe phosphine donors. For the ^{13}CO-labeled compounds, the magnitudes of $J_{\mathrm{P-C}}$ (ca. 7 and 120 Hz) in the ^{13}C{^{1}H} NMR spectra indicate the carbonyl orientation relative to dppe. While the coordinated diiodobenzene resonances are partially masked by the dppe phenyl groups, dissolution of the complexes in CD_3CN cleanly results in rapid conversion to the corresponding bis(acetonitrile) complexes **4a** and **4b** (vide infra) with concomitant liberation of 1 equiv of diiodobenzene.

Partial assignment of the coordinated diiodobenzene resonances for the two complexes was accomplished by conducting H,H-COSY experiments (see Supporting Information, Figure S.1). The doublet of doublets observed in the aromatic region [δ 6.97 and 7.39 for **3a**; δ 6.85 and 7.4 (overlapping with a phenyl resonance of dppe) for **3b**] integrate to 1H each and therefore can only belong to the diiodobenzene ligand. On the basis of this presumption, the other resonances for this ligand can also be assigned by correlation of the cross peaks in the respective H,H-correlated spectra of the two complexes.

The diiodobenzene adducts are stable solids and can be stored at room temperature for weeks with no apparent decomposition. In solution, **3a** slowly isomerizes without liberation of free diiodobenzene forming a symmetrical species (**3a′**) as evidenced by a single resonance at δ 35.20 (s) in the ^{31}P{^{1}H} NMR spectrum and a triplet ($J_{\mathrm{P-H}} = 4.0$ Hz) for the Ir−CH$_3$ group at 1.23 ppm. Observation of **3a′** commences within 20 min at room temperature. For **3b** in solution, slow decomposition is noted over several hours unless the solution is cooled or free diiodobenzene is added. While the nature of the decomposition was not elucidated, it may relate to the reactivity of the trifluoromethyl ligand when bound to a cationic metal center with adjacent labile coordination sites.[26,27]

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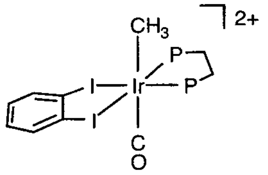
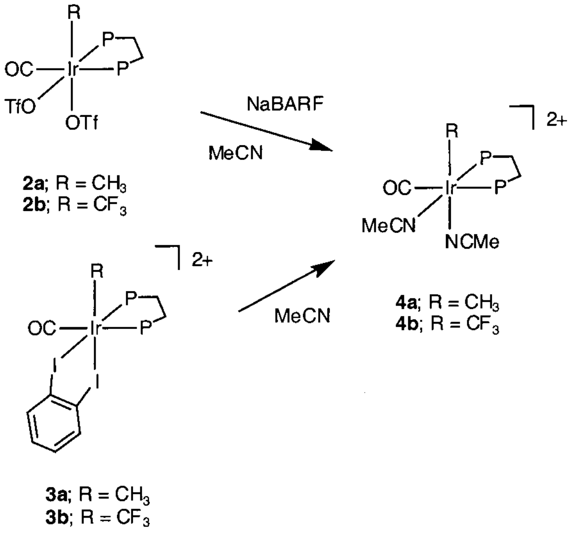


3a'

Synthesis of [IrR(CO)(dppe)(NCMe)$_2$][BARF]$_2$ Where R = CH_3 and CF_3 (4a and 4b). The MeCN adducts **4** may be generated via two pathways (eq 4). The first is similar to that used for the diiodobenzene complexes, namely, metathesis of the OTf^- ligands with $BARF^-$ in the presence of MeCN, while the second is by exchange of diiodobenzene. The latter pathway is discussed in more detail below. Acetonitrile complexes **4a** and **4b** retain the geometry of the bis(triflate) analogues as indicated by the 1:1 resonances in their $^{31}P\{^1H\}$ NMR spectra (δ 22.50 and 17.49 for **4a**; δ 22.55 and 19.50 for **4b**) and the J_{C-P} values (ca. 8 and 120 Hz) for the carbonyl ligands. The coordinated MeCN molecules are observed as singlets in the ^1H NMR spectra at δ 2.63 and 1.80 for **4a** and δ 2.78 and 1.75 for **4b**.



(4)

Due to strong coordination of MeCN, the donors exchange slowly when dissolved in acetonitrile-d_3, where the $t_{1/2}$ for the exchange process of **4b** at room temperature is approximately 1 week. Both of the coordinated MeCN molecules exchange at roughly the same rates for **4b**, whereas the upfield MeCN ligand of **4a** exchanges more rapidly than the other, presumably due to the stronger trans labilizing effect of the CH_3 ligand relative to the dppe phosphines.

Migratory insertion of CO does not occur for either **4a** or **4b** as indicated by the ν_{CO} values (2115 and 2144 cm^{-1}, respectively) and chemical shifts of CO in the $^{13}C\{^1H\}$ NMR spectra (δ 163 and 159, respectively). For comparison, the corresponding NMR and IR data for the previously reported[21,28] acyl complex are quite different ($\delta = 202$ and $\nu_{CO} = 1656$ cm^{-1}). While the lack of CO insertion was expected for the CF_3 complex **4b**, it was not for the analogous methyl complex **4a** in view of the fact that a geometric isomer of **4a** was found to undergo facile migratory insertion in a previous report. However, heating a solution of **4a** in MeCN-d_3 to 75 °C in the NMR spectrometer yielded no evidence of acyl formation.

Ligand Exchange Chemistry of Complexes 3a and 3b. The lability of coordinated diiodobenzene was examined by conducting various exchange reactions. Since acetonitrile rapidly displaces diiodobenzene at room temperature, a closer investigation at low temperatures was carried out. For **3a**, no reaction is observed below −40 °C, while for **3b**, exchange does not occur below −25 °C. The temperature difference suggests the greater lability of diiodobenzene for the Ir−CH_3 analogue **3a**. Interestingly, intermediates are observed (**4a**‡ and **4b**‡) for both processes, the resonances of which diminish with appearance of the final bis(acetonitrile) adducts **4a** and **4b**. Furthermore, free diiodobenzene is not detected in the ^1H NMR spectra until the final complexes grow in, suggesting a stepwise exchange process where the intermediate is a monodentate diiodobenzene complex (Scheme 1).

Examination of exchange using CO as the incoming ligand gave similar results. Complex **3b** exchanges with CO less rapidly and less extensively than **3a** as a result of weaker back-bonding between CO and the more electrophilic metal center. For **3a**, an initial unsymmetrical intermediate (**5a**‡) is observed at δ 33.4 and 18.3, which over the period of 3 h goes away as the tri(carbonyl) complex *fac*-$IrCH_3(CO)_3$-(dppe)$^{2+}$ (**5a**) grows in at 25.3 ppm (Figure 1). Like the exchange reactions with MeCN, free diiodobenzene is not observed until conversion to the final product begins. Exchange of CO for diiodobenzene in **3b** occurs more slowly, with complete conversion to the unsymmetrical intermediate (**5b**‡) taking ca. 2 h. Again, free diiodobenzene is not observed during this process, suggesting that it remains coordinated to the metal, but only ca. 10% (by ^{31}P NMR) of the final product *fac*-$IrCF_3(CO)_3$(dppe)$^{2+}$ (**5b**) is formed after several hours. The remaining mixture of products consists of other unidentified species as evidenced by multiple resonances in the $^{31}P\{^1H\}$ NMR spectrum and may result from the reactivity of the cation-coordinated trifluoromethyl ligand.[26,27,29]

Reactions using ^{13}CO as the incoming ligand provide additional information regarding the nature of the intermediate based on the J_{P-C} coupling constants. Starting from either **3a** or **3b**, the observed intermediate demonstrates a small J_{P-C} value (7.0 and 3.8 Hz, respectively) indicating that ^{13}CO is cis to both ^{31}P nuclei of dppe. It is also clear that the second exchange forms *fac*-IrR(CO)(^{13}CO)$_2$(dppe)$^{2+}$, which demonstrates a large J_{P-C} value ($J_{P-C} \approx 90$ Hz) supporting a trans orientation of the second ^{13}CO ligand relative to one of the ^{31}P nuclei of dppe. On the basis of these observations, the most consistent mechanism is that shown in pathway 1 of Scheme 1, where exchange initially occurs at the

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(28) The original assignment of the inserted product described in ref 21 was found incorrect as indicated by the J_{C-P} magnitudes (ca. 5−7 Hz) of the ^{13}CO analogue. Therefore, CO is cis to dppe, not trans as originally assigned.

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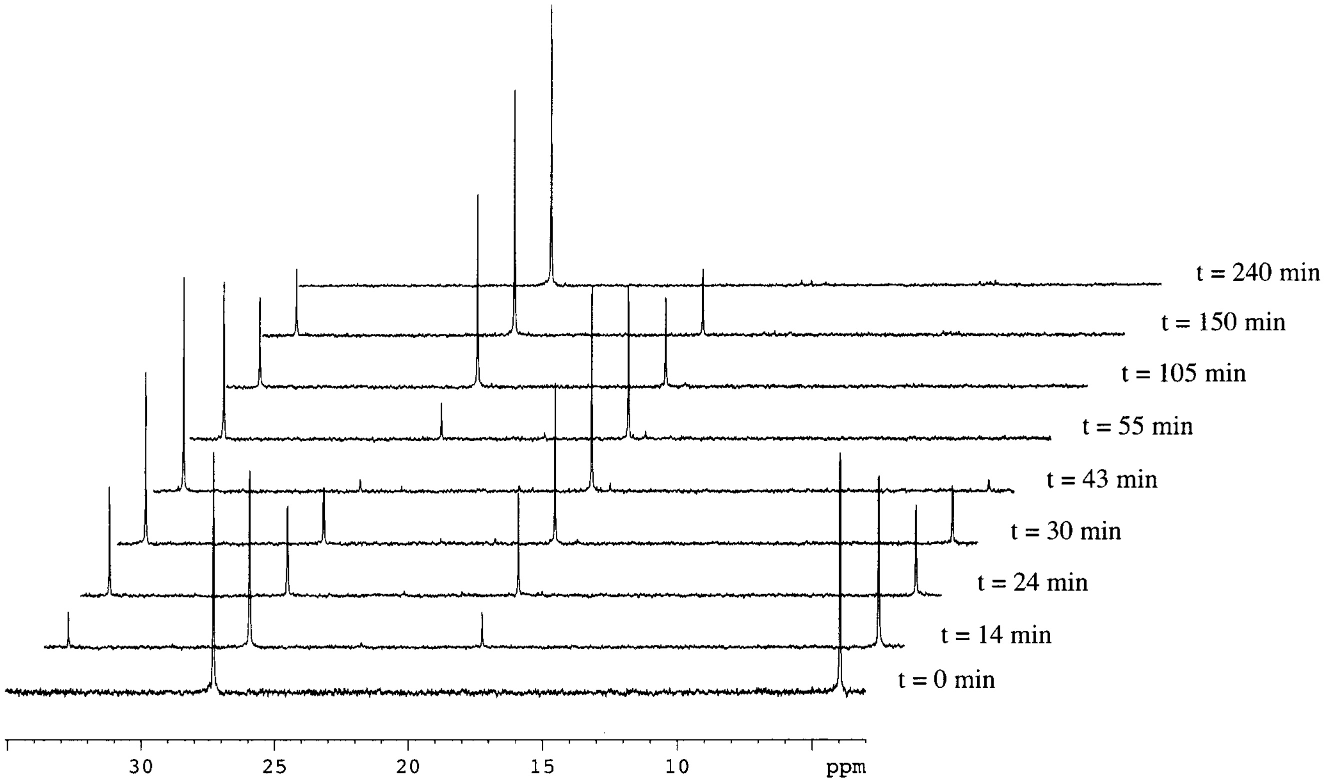
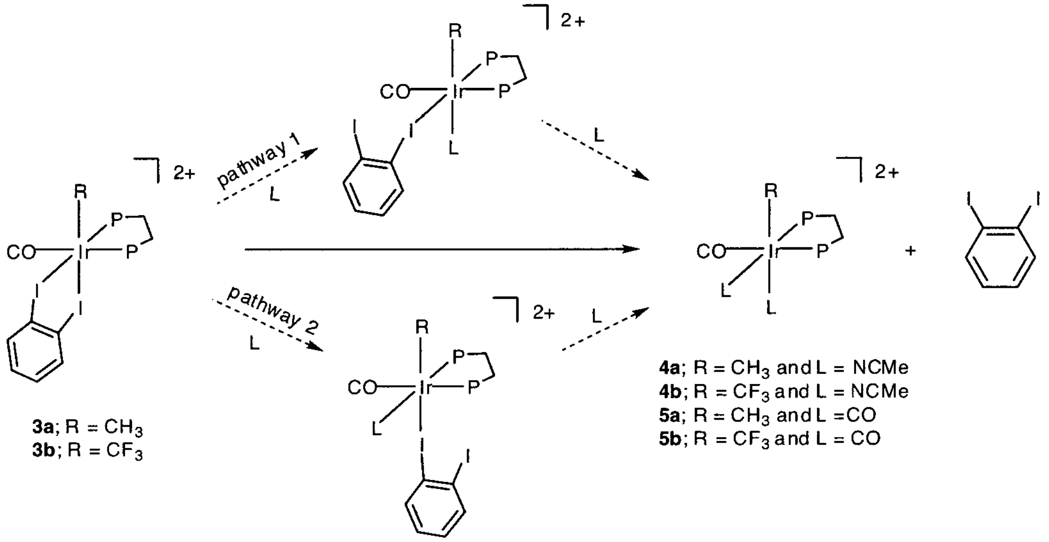


Figure 1. Time-elapsed $^{31}P\{^1H\}$ NMR spectra (gradual warming from −10 °C to room temperature) for exchange of 1,2-diiodobenzene by CO. Complex (δ): **3a** (27.28 and 3.95); **5a**‡ (33.4 and 18.3); **5a** (25.3).

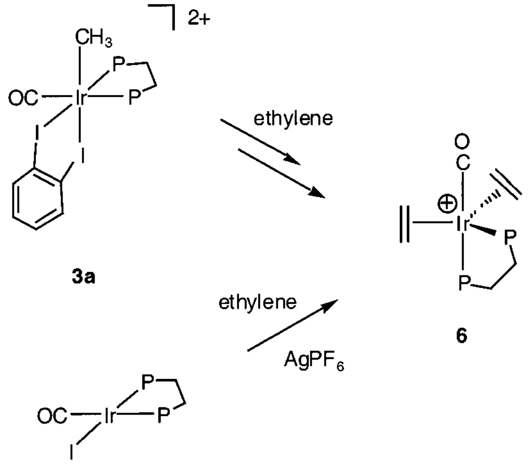
Scheme 1



coordination site trans to the iridium alkyl group due to its greater trans-directing ability. Further support for the η^1-diiodobenzene complex comes from a H,H-COSY of the intermediate **5a**‡ obtained at −20 °C (Supporting Information, Figure S.2). On the basis of the large downfield shift of one of the DIB resonances (H_1, ca. δ 7.99), the doublet of doublets coupling pattern, and the corresponding cross peaks, this resonance can be assigned as the proton adjacent to the uncoordinated iodine atom. Likewise, the reactions with MeCN appear to proceed via the same pathway as evidenced by similar chemical shifts in the $^{31}P\{^1H\}$ NMR spectra of the intermediate species. In all of the aforementioned cases, the second exchange appears to be slower than the first, indicating that loss of DIB is the rate-determining step of the reaction.

Reaction Chemistry with Ethylene. Recently reported work[22] has shown extensive reaction chemistry of the diiodobenzene adducts with different olefinic substrates, portions of which are further described below. Although **3a** does not show evidence of reaction when the simplest of the olefins (ethylene) is present in stoichiometric amounts, chemistry does occur when the latter is present in large excess (eq 5). Condensation of ethylene into a CD_2Cl_2 solution of **3a** results in formation of a new iridium complex after several days (ca. 5 days when 300 equiv is added). The major product from the reaction demonstrates a broad resonance at ca. δ 22 in the $^{31}P\{^{1}H\}$ NMR spectrum. Furthermore, a broad resonance at ca. 2.6 ppm, a second-order pattern centered at ca. 2.9 ppm [$J_{P-H} = 18$ Hz, PCH_2CH_2P], and free diiodobenzene are observed in the ^{1}H NMR spectrum. Interestingly, neither the Ir$-CH_3$ group nor any hydrides are detected. Additionally, removal of ethylene does not result in regeneration of **3a**, indicating the occurrence of further reaction after diiodobenzene exchanges with ethylene.[30]

From the broad $^{31}P\{^{1}H\}$ NMR resonance and the appearance of the dppe backbone protons as a symmetrical second-order pattern, it is reasonable to suggest that this product is a fluxional, five-coordinate Ir(I) species. Strong support for this notion was obtained from comparison of the NMR data with spectra obtained for the related analogues $IrX(CO)_2$(dppe), where X = halide or C(O)-2,4,6-$C_6H_2Me_3$.[23,31] Likewise, the broad resonance at 2.6 ppm could tentatively be assigned as the coordinated olefin. On the basis of these assumptions, independent generation of the product was pursued via a different route in an attempt to ascertain the nature of the product of the reaction of **3a** with ethylene. Halide abstraction from Ir(^{13}CO)(dppe)I using $AgPF_6$ in the presence of ethylene results in clean formation of the cationic diolefin complex **6-^{13}CO** (eq 5) with appearance and chemical shifts of the resonances identical to those obtained from the reaction of **3a-^{13}CO** with ethylene. With regard to the reduction of Ir(III) to Ir(I) in the conversion of **3a** to **6**, the exact nature of the oxidation product(s) is not clear at this time. From the reaction, butene isomers have been positively identified as byproducts using GC/MS and ^{1}H NMR spectral analyses with comparison to known standards (trace higher olefins—C_6 and C_8—are also detected by the former method). Likewise, reactions conducted with **3a-$^{13}CH_3$** demonstrate that methane is generated as the *primary* ^{13}C-labeled product with no evidence of insertion into CO or ethylene. No evidence of propylene or acetaldehyde as an oxidation byproduct is seen during the reaction.



(5)

To gain further insight into the fluxional behavior of the diolefin adduct, low-temperature NMR studies were conducted as shown in Figures 2 and 3. In the $^{31}P\{^{1}H\}$ NMR spectra, decreasing the temperature of a CD_2Cl_2 solution of **6-^{13}CO** results in initial broadening of the peak at δ 22 as the coalescence temperature ($T_c \approx -10$ °C) is approached, followed by decoalescence into two peaks at δ 25.6 and 19.7 ($J_{P-P} = 9.8$ Hz) which become increasingly sharper, revealing J_{C-P} of 7.4 and 131 Hz at ca. -70 °C (Figure 2). The results are consistent with the static structure of **6-^{13}CO** containing two distinct ^{31}P environments for dppe, with one of the phosphines trans to ^{13}CO and the other cis, which are averaged by a dynamic process.

The variable-temperature ^{1}H NMR spectra were equally informative (Figure 3). The second-order pattern at δ 2.9 representing the rapidly equilibrating dppe backbone H's (see Figure 3 inset) broadens as the temperature is decreased and decoalesces below -40 °C into two separate resonances, indicating two distinct types of dppe H's at the slow exchange limit (ca. -80 °C). ^{31}P decoupling of the ^{1}H NMR spectrum at -90 °C confirms the assignment of the dppe backbone resonances at δ 2.95 and 2.67 with $J_{P-H} = 18$ and 26 Hz, respectively.

For the coordinated ethylene resonance at ca. 2.5 ppm, sharpening is observed when the temperature is initially lowered, indicating a decrease in the rate of intermolecular exchange between free and coordinated olefin. Further cooling below 0 °C results in separation of the two overlapping ethylene resonances. The two peaks decoalesce (δ 2.54, $T_c = -60$ °C; δ 2.34, $T_c = -70$ °C) into two resonances *each* (δ 3.08 and 1.80; 2.48 and 2.20, respectively) as the slow exchange limit is approached (Figure 4b; discussed in more detail below). The observation of four distinct olefinic resonances at the slow exchange limit indicates equivalence of the two ethylene ligands due to presence of a mirror plane within **6**. At -90 °C, the six resonances (four for ethylene and two for the dppe backbone H's) in the range δ 2.95$-$1.80 integrate to 2 H's each relative to the 20 phenyl protons, supporting the assignment.

Interpretation of Variable-Temperature NMR Experiments. The variable-temperature NMR spectra suggest that averaging of the ligands coordinated to iridium is taking place via three dynamic processes. Starting from the slow exchange limit (ca. -90 °C), coalescence of the four distinct ethylene peaks (H_a, H_b, H_c, and H_d) into two sets occurs indicating equivalency of H_a/H_c and H_b/H_d as the temperature is raised. The energy barrier is ca. 9 kcal/mol based on the rate constants at the corresponding coalescence temperatures and indicates that this is the lowest energy process. Ethylene proton equilibration into two sets most likely results from "propeller" rotation,[32−35] wherein the molecule spins rapidly about the metal$-$olefin axis thereby interconverting the trans H's.

In the second dynamic process, the two P donors are interchanged, as are the dppe backbone protons and inequivalent ortho phenyl protons of the dppe ligand. The

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(30) No intermediate species are observed during the reaction.

(31) Fisher, B. J. Thesis, University of Rochester, 1983.

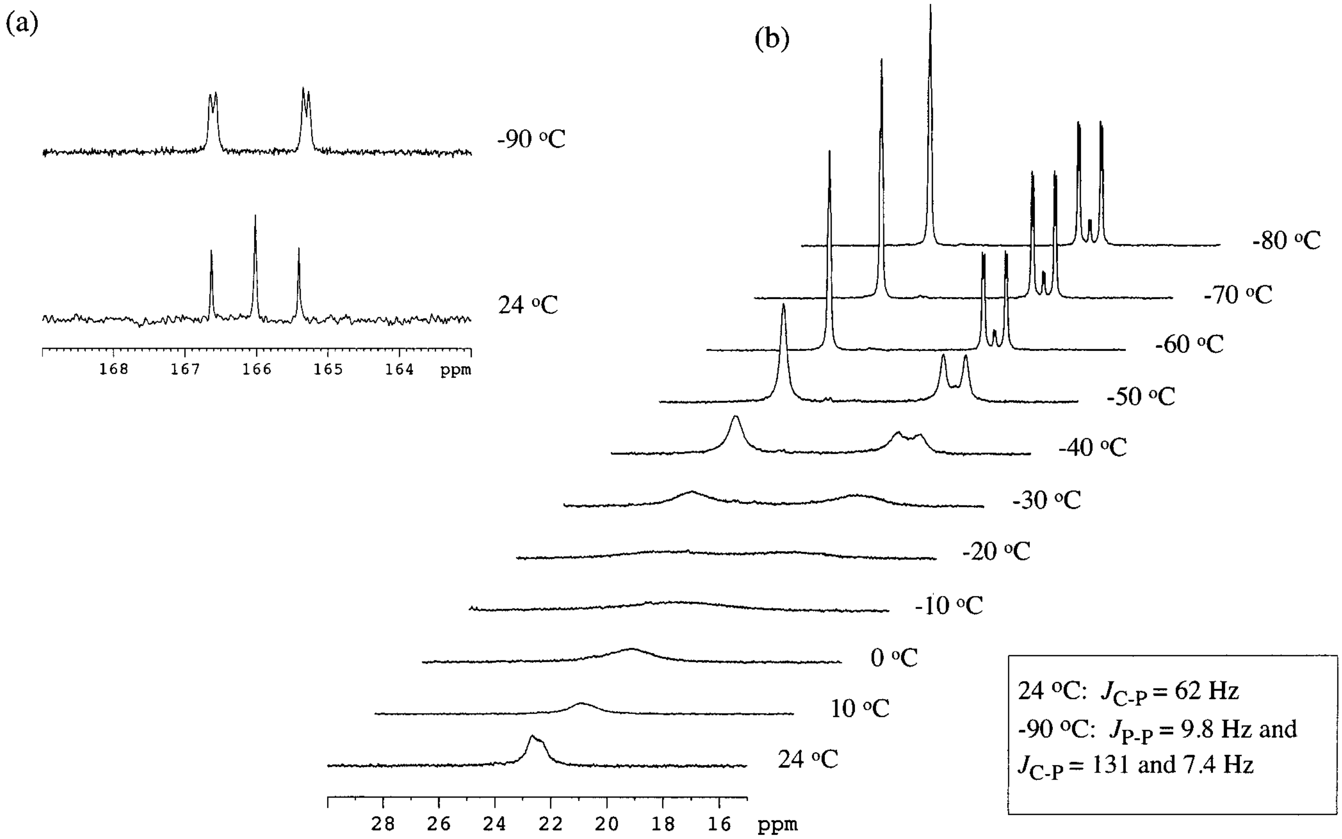

Figure 2. Low-temperature NMR spectra of complex **6-^{13}CO** in CD_2Cl_2 with 10 equiv of free ethylene in solution: (a) $^{13}C\{^1H\}$ NMR spectra of Ir−CO region at 24 and −90 °C and (b) $^{31}P\{^1H\}$ NMR spectra from 24 to −80 °C.

coalescence temperature is ca. −40 °C for the dppe backbone resonances in the ^1H NMR spectra, −40 °C for the inequivalent ortho phenyl protons, and −10 °C for the phosphine resonances in the $^{31}P\{^1H\}$ NMR spectra. On the basis of the individual coalescence temperatures and chemical shift differences from the three sources at their slow exchange limits, $\Delta G^{\pm}$ was calculated to be ca. 11 kcal/mol for this second process. The most logical mechanism of fluxionality to achieve the averaging of resonances required in the second process is Berry pseudorotation (BPR) wherein axial and equatorial positions in a trigonal bipyramid are interchanged around one equatorial site serving as a pivot. However, to interconvert axial and equatorial dppe phosphines via BPR in **6** and *retain* the same structure, three pseudorotations are required in which the other three ligands (ethylene-1, CO, ethylene-2) are each used *once* as the pivot (Figure 4a). It is interesting to note that while BPR averages equatorial and axial sites in a trigonal bipyramid, it does not serve to equilibrate all of the ethylene protons which remain in two distinct sets.

Finally, the highest energy process appears to be intermolecular exchange with free ethylene as indicated by sharpening of the coordinated ethylene resonance at 2.6 ppm when the sample is initially cooled (Figure 3, traces from 24 to 0 °C). Since the high-temperature limit was not investigated, $\Delta G^{\ddagger}$ and T_c for the process were not determined.

Simulation of NMR Spectra. In order to obtain accurate rate constants as a function of temperature for the two lower energy processes of complex **6**, NMR line shape analyses and simulations were conducted on the $^{31}P\{^1H\}$ and ^1H NMR spectra using the program Win DNMR (v 7.1.3). The simulations yielded rate constants as a function of temperature which are presented in Table 2. From these data were calculated activation parameters, and the results are presented in Table 1. Spectral simulations and Eyring and Arrhenius plots are given in the Supporting Information. The $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values for the lowest energy process of ethylene propeller rotation (~9 kcal/mol and 9.5(6) kcal/mol, respectively) are slightly lower (2−4 kcal/mol) than those reported for other Ir(I) and Ir(III) olefin complexes,[32−35] suggesting reduced metal−olefin back-bonding in **6** which is a cationic carbonyl species.

The activation parameters calculated from the $^{31}P\{^1H\}$ spectra agree with those based on the ortho phenyl proton resonances since both equilibrations occur in the same process of Berry pseudorotation. Simulation of the dppe backbone protons, which are also equilibrated in this process, was not possible with the program due to their complexity.

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(33) Yan, X.; Einstein, F. W. B.; Sutton, D. *Can. J. Chem.* **1995**, *73*, 939−955.

(34) Batchelor, R. J.; Einstein, F. W. B.; Lowe, N. D.; Palm, B. A.; Xiaoqian, Y.; Sutton, D. *Organometallics* **1994**, *13*, 2041−2052.

(35) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*; Pergamon Press: Elmsford, NY, 1982; Vol. 3.

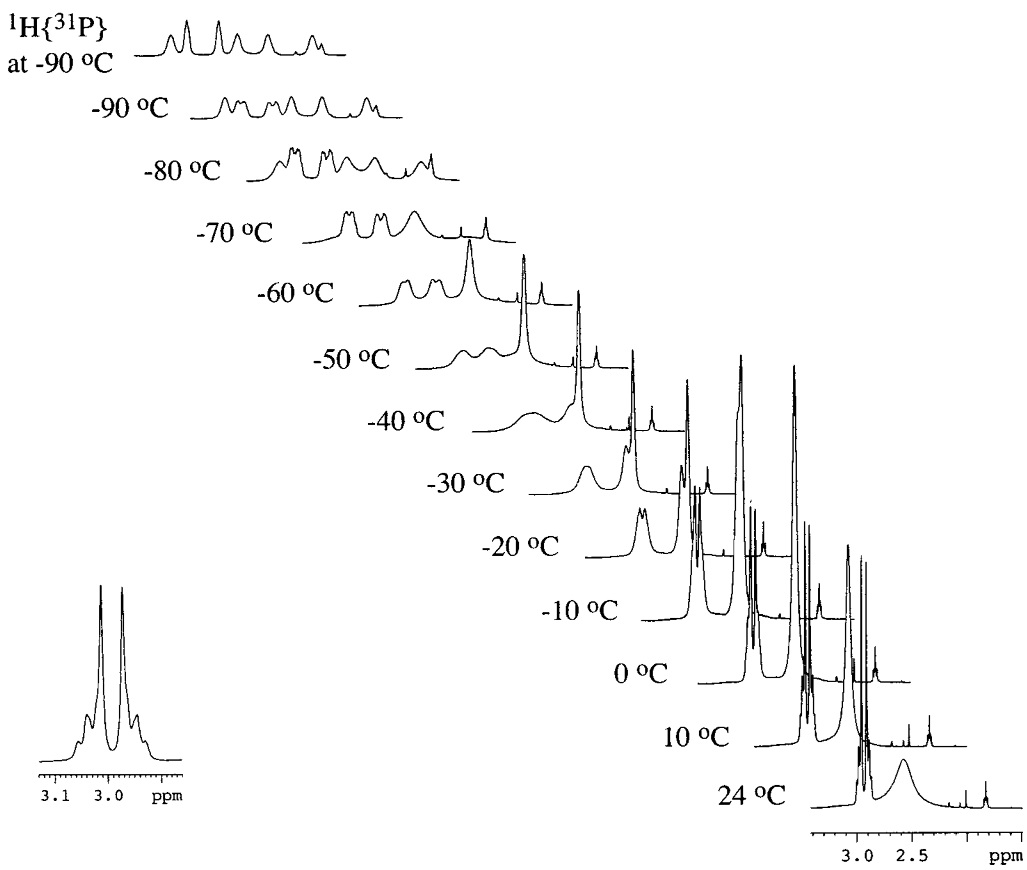

Figure 3. Low-temperature ^{1}H NMR spectra of complex **6-^{13}CO** in CD_2Cl_2 with 10 equiv of ethylene (not shown) in solution. Peaks at δ 2.9 are the dppe backbone H's (shown expanded at left), and the broad peak at δ 2.5 is coordinated ethylene. The inset shows the second-order pattern at ca. 2.9 ppm for **6-^{13}CO** more clearly [J_{P-H} = 18 Hz, PCH_2CH_2P].

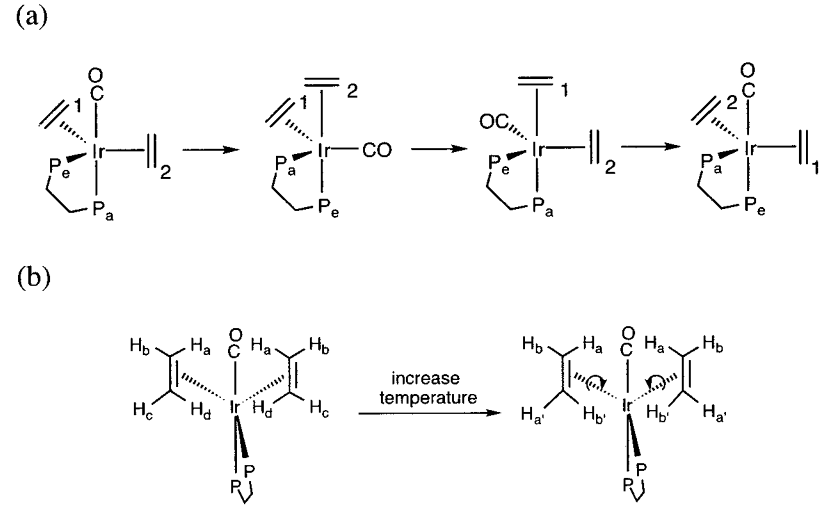

Figure 4. Proposed dynamic processes of complex **6** based on the low-temperature NMR spectra: (a) three Berry pseudorotations to equilibrate the ethylene and dppe ligands using ethylene-1, CO, and ethylene-2 as pivots, and (b) ethylene equilibration via M−olefin rotation. Intermolecular ethylene exchange is not illustrated.

The Eyring and Arrhenius plots for the BPR process are presented in the Supporting Information and yield $\Delta H^{\ddagger} \approx$ 10 kcal/mol, $\Delta S^{\ddagger} \approx -5$ eu, and $E_a \approx 10$ kcal/mol. These values are consistent with those reported in the literature,[23,35,36] and the calculated free energy barriers $\Delta G^{\ddagger}$ (ca. 11 kcal/mol) at the corresponding T_c's for phosphine donors and phenyl protons compare well with values calculated directly from the NMR spectra based on $\Delta\nu$ for the respective resonances.

For the highest energy process of intermolecular ethylene exchange, the high-temperature limit was not achieved and the data are therefore limited. However, on the basis of the temperature range 0−24 °C, the rate constants calculated

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(36) Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1067−1073.

Table 1. Activation Parameters[a] for Fluxionality of Complex **6** Starting from the Slow Exchange Limit

source	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	E_a (kcal/mol)	$k_{obs}{}^{f}$ (s^{-1}) at T_c	$\Delta G^{\ddagger}{}_{obs}{}^{g}$ (kcal/mol)	$\Delta G^{\ddagger}{}_{calc}{}^{g}$ (kcal/mol)
inner ethylene H's[b] (ethylene rotation)	9.5(6)	1(3)	9.9(6)	247 at −70 °C	9.5	9.2(5)
outer ethylene H's[c] (ethylene rotation)	9.5(6)	1(3)	9.9(6)	1.1×10^3 at −60 °C	9.3	9.2(6)
dppe backbone H's[d] (pseudorotation)				255 at −40 °C	11.0	
ortho phenylene H's (pseudorotation)	9.5(6)	−7(2)	10.0(6)	200 at −40 °C	11.1	11.1(5)
resonances from ^{31}P NMR (pseudorotation)	10.0(6)	−4(2)	10.5(6)	2.1×10^3 at −10 °C	11.3	11.2(6)
overlapping ethylene H's[e] (intermolecular exchange)	17(3)	9(9)	18(3)	2.5×10^3 >24 °C		

[a] Errors are to 90% confidence limit. [b] δ 2.48 and 2.20. [c] δ 3.08 and 1.80. [d] Could not determine $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and E_a from simulation due to the complexity of the spin system. [e] Rough estimate from intermolecular exchange between free and coordinated ethylene. [f] Based on T_c from experimental NMR spectra. [g] Values at corresponding T_c.

Table 2. Temperature Dependent Rate Constants Determined from Simulation of the Dynamic Behavior of Complex **6**

ethylene rotation		^{31}P resonances	
k (s^{-1})	T (°C)	k (s^{-1})	T (°C)
45	−90	5	−70
110	−80	25	−60
480	−70	100	−50
1300	−60	270	−40
6000	−50	610	−30
13000	−40	1240	−20
31000	−30	2800	−10
59000	−20	5000	0
		9900	10
		25000	24

ortho phenyl resonances		intermolecular exchange	
k (s^{-1})	T (°C)	k (s^{-1})	T (°C)
7	−70	16	0
25	−60	43	10
80	−50	215	24
180	−40		
360	−30		
890	−20		
2500	−10		

from the simulations lead to a rough estimate of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and E_a of 17(3) kcal/mol, 9(9) eu, and 18(3) kcal/mol, respectively, consistent with a higher energy intermolecular exchange process.

Reaction Chemistry with Substituted Olefins. Interaction of **3** with other olefins does occur and gives rise to notable and distinct chemistry, some results of which have been previously described.[22] Reaction of **3** with 1-pentene[37] results in double-bond isomerization (Scheme 2) that takes place at room temperature over several days to yield *cis*- and *trans*-2-pentene. After 5 days at room temperature, the reaction mixture corresponds to a nearly thermodynamic distribution[38] of 2% 1-pentene, 14% *cis*-2-pentene, and 84% *trans*-2-pentene under these conditions, being slightly enriched in the trans isomer. It is thought that no change in oxidation state of the metal happens during this process and therefore a mechanism similar to that proposed by Sen[39] for $Pd(NCMe)_4{}^{2+}$-induced isomerizations is assumed to be operative.

To probe further the electrophilic activities of the diiodobenzene complexes **3**, reactions with a variety of olefins were also conducted. For substrates such as styrene, β-pinene, isobutylene, α-methylstyrene, and norbornene, polymerization or oligomerization (Scheme 2) is found to occur in the presence of both **3a** and **3b**. With the exception of norbornene, addition of the respective olefin to dichloromethane solutions of the diiodobenzene complexes results in exothermic reaction in which the monomer is rapidly consumed and the solvent begins to boil. In all cases, analysis of the reaction mixtures demonstrates conversion of the monomer to polymerized or oligomerized olefin, the results of which are summarized in Table 3. Polymerizations of styrene and β-pinene lead to products that are isolated as solids, whereas isobutylene polymerizations yield viscous oils. The polyisobutylene and poly-styrene products demonstrate bimodal molecular weight distributions, explanations for which have been described in the literature.[40] For α-methylstyrene, a 1:1 ratio of the cyclized dimer and trimer (indane derivatives) is observed by ^{1}H NMR and found consistent with the reported reactivity[2,41] of α-methylstyrene with cationic initiators at or above room temperature. For norbornene, the reaction is found to be slow and gives an oily product that is soluble in low-polarity solvents, such as CH_2Cl_2 or $CHCl_3$. The extremely weak olefinic resonances in the ^{1}H NMR spectrum indicate that ring-opening processes[42,43] are not occurring. Furthermore, the complexity of a H,H-COSY of the isolated oligomer suggests that both 2,3- and 2,7-additions are occurring due to norbornyl cation formation (vide infra).

The fact that **3a** does not polymerize ethylene whereas both **3a** and **3b** *actively* promote polymerization/oligomerization of isobutylene, styrene, and β-pinene suggests that polymerization is occurring via cationic initiation rather than

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(37) Reactions of **3a** with 1-hexene also produced internal double bond isomers. The product distributions were not determined, however, due to the difficulty in resolving all of the different isomers for accurate quantification.

(38) Bond, G. C.; Hellier, M. *J. Catal.* **1965**, *4*, 1−5.

(39) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036−4038.

(40) Li, T.; Padias, A. B.; Hall, H. K. *Macromolecules* **1992**, *25*, 1387−1390.

(41) Baird, M. C. *Chem. Rev.* **2000**, *100*, 1471−1478.

(42) Jeremic, D.; Wang, Q.; Quyoum, R.; Baird, M. C. *J. Organomet. Chem.* **1995**, *497*, 43−147.

(43) Gilliom, L. R. *J. Am. Chem. Soc.* **1986**, *108*, 733−742.

Scheme 2

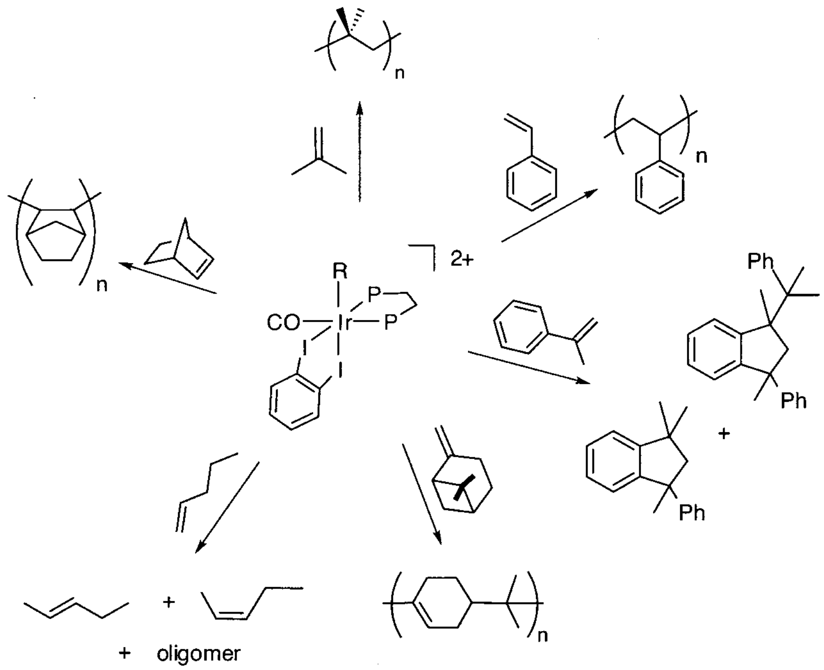

Table 3. Products Obtained from Reaction of Various Olefins with **3a** and **3b** in CH_2Cl_2

olefin	complex	M_w[a]	M_w/M_n[a]
styrene	**3a**	22200[b]	5.9
	3b	23800[b]	4.9
β-pinene	**3a**	21900	2.5
	3b	12900	2.9
isobutylene	**3a**	1940[b]	2.6
	3b	3430[b]	3.8
norbornene	**3a**	234	1.2
	3b	262	1.2
α-methylstyrene	**3a**	*c*	
	3b	*c*	

[a] Determined by SEC and referenced to polystyrene standards. [b] Bimodal molecular weight distribution. [c] 1:1 dimer:trimer.

by a coordination/insertion mechanism. The wide range of observed polydispersities supports this notion. For reactions of **3** with α-methylstyrene, formation of the indan derivatives cannot be rationalized if coordination/insertion catalysis is operative. For this substrate, reaction with a cationic initiator at room temperature generates a 3° carbocation that typically undergoes more rapid intramolecular cyclization than propagation. Furthermore, quenching of styrene polymerization with *tert*-butyl alcohol 5 s after styrene addition to a solution of **3a** results in incorporation of a *tert*-butyl ether end group[44] into the polymer chain, as evidenced by a large singlet at δ 1.26 in the ^1H NMR spectrum.

Due to the reactivities of the DIB complexes, only minor amounts are necessary for initiation resulting in unobservable metal incorporation into the polymer product under normal reaction conditions, although under other circumstances, it may be detected (vide infra). Since H^+ is liberated during chain transfer of the polymerization, the starting Ir(III) complex may be regenerated via protolysis of the Ir−C bond of the metal-bound polymer, thereby explaining the lack of initiator consumption. Further reaction (reductive elimination or *β*-hydride elimination) at the metal center may also result in removal of the metal end group from the polymer. Additionally, a kinetics argument helps to explain the absence of metal-containing end groups under normal polymerization conditions. It has been reported[45] that the rate of initiation of styrene polymerization using HOTf in 1,2-dichloroethane at 20 °C is 5−6 orders of magnitude less than the rate of chain propagation. The substantial difference in these rates results in consumption of only minor amounts of initiator, such as **3a** and **3b** in the present study.

As postulated for other sufficiently electrophilic reagents,[45−47] there are two possible mechanisms for cationic polymerization. The initiator may react either directly with the olefin to generate a carbocation or with trace H_2O resulting in generation of H^+. In view of the electrophilicities of the diiodobenzene complexes **3a** and **3b**, reaction with adventitious water cannot be completely ruled out, and indeed might be expected. If this pathway were operative, it would also explain the lack of an iridium end group on the polymer since the complexes are not directly reacting with the olefin. In order to test this notion, reactions were conducted in the presence of base[46,47] (2,6-di-*tert*-butylpyridine or Na_2CO_3) using rigorously dried reagents, but formation of polymer was still observed. While monomer consumption is slower when excess base is present,[48] complete consumption of the metal complex does occur, indicating that direct initiation happens. Moreover, evidence for an iridium end group is detected in both poly-*β*-pinene and poly-styrene by $^{31}P\{^1H\}$

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(44) Barsan, F.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1995**, No. 10, 1065−1066.

(45) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, Chichester, Brisbane, Toronto, Singapore, 1991.

(46) Moulis, J. M.; Collomb, J.; Gandini, A.; Cheradame, H. *Polym. Bull.* **1980**, *3*, 197−202.

(47) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci. Part A* **1997**, *35*, 329−344.

NMR spectroscopy for reactions carried out in the presence of an excess (4−6 equiv) of 2,6-di-*tert*-butylpyridine. For example, a $^{31}P\{^1H\}$ NMR spectrum of chromatographed polystyrene demonstrates the presence of a set of broad resonances centered at 11 ppm corresponding to the dppe phosphines after a 12 h acquisition. While *definitive* evidence supporting direct cationic initiation in the *absence* of base cannot be offered at this time, its occurrence is highly plausible on the basis of experiments in the presence of base. Further support for this view is offered by the fact that cationic initiation and polymerization by metal complexes has been seen previously for a few late metal complexes.[41]

Conclusions

In conclusion, the synthesis, characterization, and reaction chemistry of dicationic iridium(III) complexes stabilized by 1,2-diiodobenzene have been described. The complexes readily undergo exchange with acetonitrile and CO. Investigation of the exchange process demonstrates that the coordination site trans to the Ir−alkyl group is more labile, as indicated by the J_{P-C} magnitudes of the η^1-DIB intermediates when ^{13}CO is employed. Although the ν_{CO} stretch of the Ir−CF_3 analogue is consistent with a more electrophilic metal center, the stronger trans labilizing effect of the methyl group results in more facile dissociation of diiodobenzene. Finally, the diiodobenzene adducts demonstrate fairly extensive reaction chemistry with a variety of olefins. For reactions of **3a** with ethylene, reduction to a fluxional five-coordinate Ir(I) diolefin complex **6** occurs. The fluxional behavior of **6** was studied by variable-temperature NMR spectroscopy and line-shape analysis leading to rate constants and activation parameters for three processes including ethylene propeller rotation, Berry pseudorotation, and intermolecular ethylene exchange. Additional reaction chemistry with other olefins is also observed in which the diiodobenzene complexes demonstrate the ability to initiate cationic polymerization of different olefins and catalyze double-bond isomerizations of simple alkenes. The polymerization activities demonstrated by **3a** and **3b** indicate that the iridium(III) complexes behave as excellent electrophiles.

Experimental Section

General Procedures and Materials. Trifluoromethyl iodide, silver(I) triflate (AgOTf, 99.95%), silver(I) hexafluorophosphate ($AgPF_6$), 1,2-diiodobenzene, styrene, (1*S*)-(−)-β-pinene, α-methylstyrene, norbornene, pentene isomers, and 2,6-di-*tert*-butylpyridine were purchased from Aldrich Chemical Co. Styrene was distilled over CaH_2 and then filtered through activated Al_2O_3 before use. 1-Pentene, α-methylstyrene, β-pinene, 1,2-diiodobenzene, and 2,6-di-*tert*-butylpyridine were degassed, filtered through activated Al_2O_3, and then stored in an N_2-filled glovebox over activated molecular sieves. Acetonitrile-d_3 and dichloromethane-d_2 were purchased from Cambridge Isotope in ampules and filtered through activated alumina before use. Molecular sieves and alumina were thoroughly washed with CH_2Cl_2 and then activated by heating with a Bunsen burner under vacuum. $IrCH_3(CO)(dppe)I_2$,[23] $IrCH_3(CO)(dppe)(OTf)_2$,[21] and NaBARF[49] were synthesized according to published procedures. All ^{13}CO-labeled complexes were prepared according to the same procedures described below for the unlabeled analogues starting from Ir(^{13}CO)(dppe)I.[50]

Unless otherwise stated, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere using either standard Schlenk techniques or an inert-atmosphere glovebox. THF, CH_2Cl_2, hexanes, pentane, and acetonitrile were purified as described by Grubbs.[51] All NMR spectra were recorded on a Bruker AMX or Avance 400 MHz spectrometer. ^{1}H and ^{13}C chemical shifts (δ in ppm) are relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances. ^{31}P chemical shifts (δ in ppm) are relative to an external 85% solution of phosphoric acid in the appropriate solvent. ^{19}F chemical shifts (δ in ppm) are referenced externally to $CF_3C_6H_5$ in the appropriate solvent. Column chromatography on $IrCF_3(CO)(dppe)I_2$ was done using a Biotage Flash 40 system under 20 psi of nitrogen pressure. GC analyses on the pentene isomers were conducted using a Shimadzu model 17C system (oven = 8 °C, injector = 26 °C, detector = 49 °C, helium flow rate = 0.3 mL/min) fitted with a 15 m Restek Rtx-5 column (Crossbond 5% diphenyl−95% dimethyl polysiloxane, 0.25 mm i.d., 0.25 μm df). Assignments of the pentene double-bond isomers were established using standards purchased from Aldrich Chemical Co. The polymers were analyzed by size-exclusion chromatograph (SEC) in uninhibited THF using three Polymer Laboratories 7.5 mm × 300 mm Plgel mixed-C columns at room temperature and referenced to polystyrene standards. Elemental analyses were obtained from Quantitative Technologies, Inc., Whitehouse, NJ. Mass spectrometry data were obtained on an Hewlett-Packard series 1100 MSD fitted with an atmospheric pressure ionization chamber.

The NMR simulations were conducted using the program Win DNMR version 7.1.3, which was written by Hans J. Reich from the Department of Chemistry of the University of Wisconsin, Madison. The additional program Win NUTS version 5.093 was also used to process the NMR spectra before importing them into Win DNMR. For conducting the simulations, the spectra obtained at the slow exchange limit were initially used to determine the peak positions, peak widths, coupling constants, and relative peak percentages where applicable. These values were used as the default values in the absence of any exchange. The following are the parameters at the slow exchange limits used for each of the 4 simulations: intermolecular exchange for a 2-spin system [free ethylene, width = 3.0 Hz, intensity = 90%] and [coordinated ethylene peak, width = 8.8 Hz, intensity = 10%]; ortho phenyl H's [spin system simplified to ABX_2 where $J_{AB} = 0$ and $J_{X_2} \approx J_{PH} \approx J_{HH} \approx 8.2$ Hz, peak widths = 7.1 Hz]; $^{31}P\{^1H\}$ NMR equilibration [spin system used is ABX where $J_{AB} = 9.9$ Hz, $J_{AX} = 6.7$ Hz, and $J_{BX} = 130.7$ Hz, peak widths = 5.8 Hz]; ethylene rotation [used a 4-spin system with 1:1:1:1 ratio for the 4 peaks, peak widths = 10.8 Hz].

Synthesis of the Iridium Complexes. A. Synthesis of $IrCF_3(CO)(dppe)I_2$ (1b, 1c, and 1d). A 25 mL Schlenk flask equipped with a stir-bar was charged with IrI(CO)(dppe) (749 mg, 1 mmol) and 14 mL of CH_2Cl_2. The solution was cooled to −78 °C, and trifluoromethyl iodide was bubbled through the solution. After the

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(48) Slower polymerization should be expected in the presence of base due to its interference with the chain termination/transfer events since these entail H^+ evolution. Reactions conducted between **3a** and styrene in the presence of 2 equiv of 2,6-di-*tert*-butylpyridine were still exothermic. Slow monomer consumption was observed only when a large excess of base was used.

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reaction mixture turned red, the solution was purged with trifluoromethyl iodide for an additional 40 s. The reaction mixture was stirred at −78 °C for 10 min before removal of the low-temperature bath. After 45 min, the yellow solution was concentrated to approximately 5 mL in vacuo, and hexanes were added, resulting in precipitation of a cream-colored solid. The solid was isolated in air on a frit washing with hexanes yielding 883 mg of a mixture of isomers (ca. 90% **1b**). The material was dissolved in 5 mL of CH_2Cl_2 and injected onto a Biotage 40M cartridge (KP-Sil, 32−63 μm, 60 Å) eluting with 1:1 hexanes/CH_2Cl_2. The kinetic isomer **1b** was the first yellow fraction off the column. After confirmation of the purity of the collected fractions, they were combined and concentrated until precipitation occurred. A yield of 730 mg (77%) of pure **1b** was obtained as a yellow solid. Concentration of the second yellow fraction from the column afforded 76 mg of primarily the thermodynamic isomer **1c**, in addition to minor amounts of **1d** and *fac*-Ir(CO)(dppe)I_3. Spectral information for **1b**: ^{1}H NMR (CD_2Cl_2) δ 7.20−8.20 (20H, phenyl), 3.10−3.40 (overlapping m, 4H, PCH_2CH_2P); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 13.28 (qd, $J_{P-P} = 3.9$ Hz, $J_{F-P} = 8.7$ Hz, 1P, cis to CO), −10.52 (qd, $J_{P-P} = 3.9$ Hz, $J_{F-P} = 5.3$ Hz, 1P, trans to CO); ^{19}F NMR (CD_2Cl_2) δ 62.95 (dd, $J_{P-F} = 8.7$ and 5.3 Hz, Ir−CF_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 164 (virtual dqn, $J_{P-C} = 139.7$ and 5.7 Hz, $J_{F-C} = 5.7$ Hz, CO); IR (CH_2Cl_2) 2088 cm^{-1} (CO). Anal. Calcd for $C_{28}H_{24}F_3I_2P_2OIr$: C, 35.72; H, 2.57. Found C, 35.78; H, 2.45. Spectral information for **1c**: ^{1}H NMR (CD_2Cl_2) δ 7.20−8.10 (20H, phenyl), 2.65−3.40 (overlapping m, 4H, PCH_2CH_2P); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 4.17 (qd, $J_{P-P} = 7$ Hz, $J_{F-P} = 8.7$ Hz, 1P, cis to CF_3), −16.23 (qd, $J_{P-P} = 7$ Hz, $J_{F-P} = 48$ Hz, 1P, trans to CF_3); ^{19}F NMR (CD_2Cl_2) δ 61.51 (dd, $J_{P-F} = 48$ and 8.7 Hz, Ir−CF_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 154.5 (qdd, $J_{P-C} = 3.8$ and 6.0 Hz, $J_{F-C} = 4.0$ Hz, CO); IR (CH_2Cl_2) 2068 cm^{-1} (CO). Spectral information for **1d**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 8.15 (q, $J_{F-P} = 6.7$ Hz, 2P, cis to CF_3); ^{19}F NMR (CD_2Cl_2) δ 54.35 (t, $J_{P-F} = 6.7$ Hz, Ir−CF_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 165.4 (qt, $J_{P-C} = 4.6$ Hz, $J_{F-C} = 16.5$ Hz, CO).

B. Synthesis of $IrCF_3(CO)(dppe)(OTf)_2$ (2b). A similar procedure was followed as described for the synthesis of **2a**.[21] A 100 mL round-bottom flask containing a stir-bar was charged with AgOTf (131 mg, 0.51 mmol) and 32 mL of CH_2Cl_2 in the dark. $IrCF_3(CO)(dppe)I_2$ (231 mg, 0.25 mmol) was added as a solid to the suspension followed by 4 mL of CH_2Cl_2. After 5 min, AgI began to precipitate out of solution. The reaction mixture was stirred for 3.5 h. An aliquot was removed, and a $^{31}P\{^1H\}$ NMR spectrum was obtained indicating that the reaction was complete. The AgI solid was removed by gravity filtration through a medium-porosity frit revealing a near colorless solution. The filtrate was concentrated in vacuo, leaving a white solid. If necessary, any yellow impurities may be removed by washing the product with the minimum amount of cold CH_2Cl_2 at −40 °C. Isolated: 203 mg (84%). ^{1}H NMR (CD_2Cl_2): δ 7.47−7.90 (20H, phenyl), 3.10−3.40 (overlapping m, 4H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.39 (virtual qn, $J_{P-P} = J_{F-P} = 6.1$ Hz, 1P, trans to CO), 11.21 (m, difficult to resolve, 1P, cis to CO). ^{19}F NMR (CD_2Cl_2): δ 55.88 (m, difficult to resolve, 3F, Ir−CF_3), −13.62 (m, difficult to resolve, 3F, OTf), −14.30 (q, $J_{F-F} = 2.2$ Hz, 3F, OTf). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.2 (virtual dqn, $J_{P-C} = 130$ and 6.1 Hz, $J_{F-C} = 6.1$ Hz, CO). IR (CH_2Cl_2): 2132 cm^{-1} (CO). Anal. Calcd for $C_{30}H_{24}F_9O_7P_2S_2Ir\cdot CH_2Cl_2$: C, 34.77; H, 2.45. Found C, 34.82; H, 2.21.

C. Synthesis of $[IrCH_3(CO)(dppe)(DIB)][BARF]_2$ (3a) Where DIB = 1,2-Diiodobenzene. A 50 mL round-bottom flask equipped with a stir-bar was charged with $IrCH_3(CO)(dppe)(OTf)_2$ (240 mg, 258 μmol), 10 mL of CH_2Cl_2, and 1,2-diiodobenzene (100 μL, 765 μmol). NaBARF (683 mg, 771 μmol) was then added as a solid to the rapidly stirred solution followed by an additional 5 mL of CH_2Cl_2. After 5 min, the solid NaOTf was removed by filtration and the solution was concentrated in vacuo to 5 mL, at which point 15 mL of hexanes was added. The solvent was concentrated to 10 mL and decanted from the oil. After the oil was dried in vacuo, the resulting solid was thoroughly washed with hexanes and dried, leaving an off-white solid. Additional washings with hexanes may be necessary to completely remove any residual 1,2-diiodobenzene. Crude yield: 582 mg (84%). The material may be purified if necessary by successive recrystallizations from CH_2Cl_2/hexanes and filtrations to remove any remaining sodium salts. Purified yield: 510 mg (73%). ^{1}H NMR (CD_2Cl_2): δ 7.42−7.85 (overlapping, 39H, phenyl, BARF), 7.39 (dd, $J_{meta} = 1.3$ Hz, $J_{ortho} = 8.2$ Hz, 1H, DIB), 7.25 (overlapping, 3H, phenyl), 7.11 (td, $J_{meta} = 1.3$ Hz, $J_{ortho} = 8.0$ Hz, 1H, DIB), 7.03 (overlapping, 3H, phenyl), 6.97 (dd, $J_{meta} = 1.3$ Hz, $J_{ortho} = 8.2$ Hz, 1H, DIB), 3.60 (overlapping m, 2H, PCH_2CH_2P), 2.97 (overlapping m, 2H, PCH_2CH_2P), 1.05 (dd, $J_{P-H} = 5.3$ and 3.1 Hz, 3H, for $^{13}CH_3$ complex, $J_{C-H} = 140.6$ Hz, Ir−CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 27.28 (d, $J_{P-P} = 3.6$ Hz, 1P, cis to CO), 3.95 (d, $J_{P-P} = 3.6$ Hz, 1P, trans to CO). ^{19}F NMR (CD_2Cl_2): δ 0.24 (s, BARF). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.7 (dd, $J_{P-C} = 122$ and 7.1 Hz, CO), −10.4 (t, $J_{P-C} = 4.2$ Hz, for ^{13}CO and $^{13}CH_3$ complex, $J_{C-C} = 1.8$ Hz, Ir−CH_3). IR (thin film): 2106 cm^{-1} (CO). Anal. Calcd for $C_{98}H_{55}B_2F_{48}I_2P_2OIr\cdot$hexanes: C, 44.99; H, 2.51. Found C, 44.82; H, 2.57. Slow isomerization from **3a** to **3a′** in CH_2Cl_2 begins after ca. 10 min at room temperature. Spectral information for **3a′**: ^{1}H NMR (CD_2Cl_2) δ 1.23 (t, $J_{P-H} = 4.0$ Hz, 3H, for $^{13}CH_3$ complex, $J_{C-H} = 133.1$ Hz, Ir−CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 35.20 (s, 2P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 164.6 (t, $J_{P-C} = 4.5$ Hz; for ^{13}CO and $^{13}CH_3$ complex, $J_{C-C} = 25.1$ Hz, CO), −4.98 (t, $J_{P-C} = 5.4$ Hz; for ^{13}CO and $^{13}CH_3$ complex, $J_{C-C} = 25.1$ Hz, Ir−CH_3).

D. Synthesis of $[IrCF_3(CO)(dppe)(DIB)][BARF]_2$ (3b) Where DIB = 1,2-Diiodobenzene. The same procedure was followed as described above for the synthesis of **3a**. $IrCF_3(CO)(dppe)(OTf)_2$ (357 mg, 0.362 mmol), 1,2-diiodobenzene (145 μL, 1.11 mmol), NaBARF (965 mg, 1.09 mmol), and 25 mL of CH_2Cl_2 were used. Purified yield: 775 mg (78%). ^{1}H NMR (CD_2Cl_2): δ 7.5−7.98 (overlapping, 39H, phenyl, BARF), 7.36 (overlapping, 3H, phenyl), 7.28 (td, $J_{meta} = 1.4$ Hz, $J_{ortho} = 8.2$ Hz, 1H, DIB), 7.13 (td, $J_{meta} = 1.4$ Hz, $J_{ortho} = 7.4$ Hz, 1H, DIB), 7.00 (overlapping, 3H, phenyl), 6.85 (dd, $J_{meta} = 1.4$ Hz, $J_{ortho} = 8.2$ Hz, 1H, DIB), 3.75 (overlapping m, 2H, PCH_2CH_2P), 3.38 (m, 1H, PCH_2CH_2P), 3.13 (m, 1H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 25.74 (qd, $J_{P-P} = 1.5$ Hz, $J_{F-P} = 4.8$ Hz, 1P, cis to CO), −1.20 (qd, $J_{P-P} = 1.5$ Hz, $J_{F-P} = 4.1$ Hz, 1P, trans to CO). ^{19}F NMR (CD_2Cl_2): δ 70.45 (dd, $J_{P-F} = 4.8$ and 4.1 Hz, 3F, Ir−CF_3), 0.24 (s, 48F, BARF). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.8 (virtual dqn, $J_{P-C} = 117.4$ and 6.7 Hz, $J_{F-C} = 6.7$ Hz, CO). IR (thin film): 2133 cm^{-1} (CO). Anal. Calcd for $C_{98}H_{52}B_2F_{51}I_2P_2OIr$; C, 42.90; H, 1.91. Found C, 43.06; H, 1.79.

E. Generation of $[IrR(CO)(dppe)(NCCH_3)_2][BARF]_2$ Where R = CH_3 and CF_3 (4a and 4b). Complexes **4a** and **4b** were generated in NMR tubes following the two representative procedures described below. **Procedure 1.** A resealable NMR tube was charged with $[IrCH_3(CO)(dppe)(DIB][BARF]_2$ (10 mg, 3.7 μmol) and 0.5 mL of CD_2Cl_2. To the colorless solution was added CH_3CN (1 μL, 19.1 μmol). ^{1}H NMR spectral analysis of the solution demonstrated 1 equiv of free 1,2-diiodobenzene, the presence of two coordinated acetonitrile resonances, and free acetonitrile at δ 1.95. **Procedure 2.** A resealable NMR tube was charged with $IrCH_3(CO)(dppe)(OTf)_2$ (11 mg, 11.8 μmol) and 0.25 mL of CD_2Cl_2. To the suspension were added ca. 2.5 μL of CH_3CN and NaBARF

(31.4 mg, 35.4 μmol). CD_2Cl_2 (0.25 mL) was added, and the NMR tube was sealed and shaken vigorously. Analysis of the solution demonstrated conversion to the same product as observed above. A ^{19}F NMR spectrum also confirmed that complete metathesis had occurred as evidenced by the absence of any OTf^- resonances (NaOTf precipitate observed) and the presence of the CF_3 groups for the BARF counterion. (J_{P-C} values were determined using ^{13}CO-enriched samples of **4a**/**b**.) Spectral information for **4a**: ^{1}H NMR (CD_2Cl_2) δ 7.43−7.72 (overlapping, 44H, phenyl, BARF), 3.00−3.50 (overlapping m, 4H, PCH_2CH_2P), 2.63 (s, 3H, $NCCH_3$), 1.80 (s, 3H, $NCCH_3$), 0.30 (dd, J_{P-H} = 6.3 and 3.2 Hz, 3H, Ir−CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 22.50 (d, J_{P-P} = 4.9 Hz, 1P, trans to CO), 17.49 (d, J_{P-P} = 4.9 Hz, 1P, cis to CO); ^{19}F NMR (CD_2Cl_2) δ 0.24 (s, BARF); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 163 (dd, J_{P-C} = 123 and 8.1 Hz, CO); IR (thin film) 2115 cm^{-1} (CO). Spectral information for **4b**: ^{1}H NMR (CD_2Cl_2) δ 7.46−7.76 (overlapping, 44H, phenyl, BARF), 3.09−3.70 (overlapping m, 4H, PCH_2CH_2P), 2.78 (s, 3H, $NCCH_3$), 1.75 (s, 3H, $NCCH_3$); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 22.55 (qd, J_{P-P} = 1.9 Hz, J_{F-P} = 5.9 Hz, J_{C-P} = 115 Hz, 1P, trans to CO), 19.50 (m, J_{P-P} = 1.9 Hz, J_{F-P} = 5.6 Hz, 1P, cis to CO); ^{19}F NMR (CD_2Cl_2) δ 54.8 (dd, J_{P-F} = 5.9 and 5.6 Hz, 3F, Ir−CF_3), 0.24 (s, 48F, BARF); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 159 (dqn, J_{P-C} = 115 and 5.6 Hz, CO); IR (thin film) 2144 cm^{-1} (CO).

F. General Procedure for Low-Temperature Studies of MeCN Exchange Reaction with 3a and 3b. Observation of Intermediate Species 4a‡ and 4b‡. A resealable NMR tube containing either complex **3a** or **3b** (5 μmol) and CD_2Cl_2 was freeze−pump−thawed three times. A large excess (>20×) of MeCN was then vacuum transferred into the NMR tube, and the sample was kept frozen at 77 K. The probe in the NMR spectrometer was cooled to −85 °C. After slightly thawing the NMR tube, it was inserted into the probe. The reaction was then monitored while the temperature was gradually increased. Spectral information for intermediate species **4a‡** (−40 °C): ^{1}H NMR (CD_2Cl_2): δ 0.26 (unresolved coupling, 3H, Ir−CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 31.9 (1P, unresolved coupling), 17.9 (1P, unresolved coupling). Spectral information for intermediate species **4b‡** (−25 °C): ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 31.3 (1P, unresolved coupling), 12.7 (1P, unresolved coupling). ^{19}F NMR (CD_2Cl_2): δ 61.8 (3F, unresolved coupling, Ir−CF_3), 0.24 (s, 48F, BARF).

G. General Procedure for CO (or ^{13}CO) Exchange with 3a and 3b. Generation of [*fac*-IrR(CO)$_3$(dppe)][BARF]$_2$ Where R = CH_3 and CF_3 (5a and 5b). Observation of Intermediates 5a‡ and 5b‡. A resealable NMR tube containing either complex **3a** or **3b** (5 μmol) and CD_2Cl_2 was freeze−pump−thawed three times. The NMR tube was back-filled with CO at 77 K and then thawed to room temperature. The reaction was periodically monitored over the next day. Spectral information for complex **5a** (100% conversion by NMR): ^{1}H NMR (CD_2Cl_2) δ 7.45−7.77 (overlapping, 44H, phenyl, BARF), 3.54 (overlapping m, 2H, PCH_2CH_2P), 3.33 (overlapping m, 2H, PCH_2CH_2P), 0.34 (t, J_{P-H} = 6 Hz, 3H, Ir−CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 25.3 (s, 2P, J_{P-C} trans for ^{13}CO reaction = 93.8 Hz); IR (thin film) 2179 cm^{-1} (CO), overlapping at 2142 cm^{-1} (CO). Spectral information for intermediate species **5a‡** (0 °C): ^{1}H NMR (CD_2Cl_2) δ 8.02 (dd, J_{meta} = 1.5 Hz, J_{ortho} = 7.9 Hz, 1H, DIB), 7.43−7.90 (overlapping, 39H, phenyl, BARF), 7.36 (dd, J_{meta} = 1.2 Hz, J_{ortho} = 8.0 Hz, 1H, DIB), 7.31 (td, J_{meta} = 1.3 Hz, J_{ortho} = 7.5 Hz, 1H, DIB), 7.17 (td, J_{meta} = 1.6 Hz, J_{ortho} = 7.7 Hz, 1H, DIB), 3.45 (overlapping m, 2H, PCH_2CH_2P), 3.13 (overlapping m, 2H, PCH_2CH_2P), 0.61 (dd, J_{P-H} = 6.7 and 3.5 Hz, 3H, Ir−CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 33.4 (unresolved P−P coupling, 1P), 18.3 (unresolved P−P coupling, J_{C-P} = 7 Hz, 1P). Spectral information for complex **5b**:[52] ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 27 (s, 2P, J_{P-C} trans for ^{13}CO reaction = 88.6 Hz); ^{19}F NMR (CD_2Cl_2) δ 60.5 (t, J_{P-F} = 4.6 Hz, 3F, Ir−CF_3), 0.24 (s, 48F, BARF). Spectral information for intermediate species **5b‡**: ^{1}H NMR (CD_2Cl_2): δ 8.03 (dd, J_{meta} = 1.5 Hz, J_{ortho} = 7.9 Hz, 1H, DIB), 7.43−7.95 (overlapping, 39H, phenyl, BARF), 7.31 (td, J_{meta} = 1.4 Hz, J_{ortho} = 7.8 Hz, 1H, DIB), 7.23 (dd, J_{meta} = 1.4 Hz, J_{ortho} = 8.2 Hz, 1H, DIB), 7.13 (td, J_{meta} = 1.6 Hz, J_{ortho} = 7.4 Hz, 1H, DIB), 3.71 (overlapping m, 2H, PCH_2CH_2P), 3.41 (m, 1H, PCH_2CH_2P), 3.21 (m, 1H, PCH_2CH_2P); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 32.7 (virtual qn, J_{P-P} = J_{C-P} = 3.8 Hz, 1P), 15.7 (virtual qn, J_{P-P} = J_{C-P} = 3.8 Hz, 1P); ^{19}F NMR (CD_2Cl_2) δ 58.1 (virtual t, J_{P-F} = 3.8 Hz, 3F, Ir−CF_3), 0.24 (s, 48F, BARF).

Reactions with Olefinic Substrates. A. Reaction of 3a with Ethylene. A resealable NMR tube was charged with **3a** (10 mg, 3.7 μmol) and 0.5 mL of CD_2Cl_2. The solution was freeze−pump−thawed 3×, and then ethylene was condensed into the NMR tube at 77 K. The valve was closed, and the solution was carefully thawed. The reaction was then monitored periodically over a period of several days. The reaction time was found to depend on the amount of ethylene added. For reactions where 200 equiv was added, complete conversion took 5 days at room temperature. See below for NMR spectral information of the product.

B. Reaction of Ir(^{13}CO)(dppe)I with $AgPF_6$ in the Presence of Ethylene. A resealable NMR tube was charged with $AgPF_6$ (5.6 mg, 22 μmol) and Ir(^{13}CO)(dppe)I (15 mg, 20 μmol) in the dark. The NMR tube was connected to the vacuum line and evacuated. After 0.5 mL of CD_2Cl_2 was vacuum transferred into the NMR tube, ethylene was condensed into it at 77 K. The valve was closed, and the solution was carefully thawed. The NMR tube was then shaken vigorously. NMR spectral analysis after 30 min demonstrated clean conversion to **6-^{13}CO**. Spectral information at room temperature for complex **6-^{13}CO**: ^{1}H NMR (CD_2Cl_2) δ 7.53−7.60 (overlapping, 12H, meta and para phenyl H's), 7.50−7.45 (m, 8H, ortho phenyl H's), 2.93 (d with outer coupling, J_{P-H} = 16 Hz, 4H, PCH_2CH_2P), 2.56 (b, 8H, ethylene); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 22.0 (b, 2P); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 166 (t, J_{P-C} = 62 Hz, CO). Spectral information at −90 °C for complex **6-^{13}CO**: ^{1}H NMR (CD_2Cl_2) δ 7.44−7.57 (overlapping, 12H, meta and para phenyl H's), 7.43 (t, 4H, ortho phenyl H's), 7.20 (t, 4H, ortho phenyl H's), 3.08 (b, 2H, ethylene), 2.95 (d, J_{P-H} = 18 Hz, 2H, PCH_2CH_2P), 2.67 (d, J_{P-H} = 26 Hz, 2H, PCH_2CH_2P), 2.48 (b, 2H, ethylene), 2.20 (b, 2H, ethylene), 1.80 (b, 2H, ethylene); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 25.6 (dd, J_{P-P} = 9.8 Hz, J_{C-P} = 7.4 Hz, 1P, cis to CO), 19.7 (dd, J_{P-P} = 9.8 Hz, J_{C-P} = 131 Hz, 1P, trans to CO); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 166 (dd, J_{P-C} = 131 and 7.4 Hz, CO).

C. Isomerization of 1-Pentene Using 3a. A resealable NMR tube was charged with **3a** (10 mg, 3.7 μmol) and 0.6 mL of CD_2Cl_2. 1-Pentene (20 μL, 183 μmol, 50 equiv) was then added via microliter syringe, and the NMR tube was sealed and shaken. The NMR tube was then put into an agitator at room temperature and monitored periodically for 1 week. After 5 days, the ratios of the pentene isomers remained constant. After 1 week, the solvent and pentene isomers were vacuum transferred into a round-bottom flask and then analyzed by GC. The assignments of the isomers were made by comparison to known standards. A ^{1}H NMR spectrum of the nonvolatile residue remaining in the original NMR tube demonstrated the presence of an organic product consistent with oligomerized 1-pentene.[53]

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(52) For **5b**, only approximately 10% of the product is formed by NMR. The remainder of the material decomposes over time into numerous unidentified species.

D. General Procedure for Polymerization of Styrene and (1*S*)−(−)-*β*-Pinene Using 3a or 3b. A 25 mL round-bottom flask containing a stir-bar was charged with 4 mL of CH_2Cl_2 and (1*S*)−(−)-*β*-pinene or styrene (1.27 mmol, 230 equiv). Either **3a** or **3b** (5.5 μmol) was then added to the solution as a solid, resulting in an exothermic reaction and eventually an orange-colored solution. The solution was stirred for 10 min, and ^{1}H NMR spectral analysis confirmed consumption of the monomer (an NMR tube scale reaction demonstrated complete consumption of the same number of equivalents of the monomer in <3 min; reactions conducted using more concentrated solutions were extremely exothermic). The reaction mixture was then quenched with MeOH, resulting in precipitation of a white solid. The solid was isolated on a frit washing with MeOH. Typical yields were approximately 85% of a white solid whose ^{1}H NMR spectrum matched that reported in the literature (poly-styrene[54] and poly-*β*-pinene[55]). Reactions were also conducted in a similar manner in the presence of 2,6-di-*tert*-butylpyridine. When a large excess of base was employed, polymerizations were expectedly slower and therefore necessitated longer reaction times. After several hours, the reaction mixtures were quenched with methanol and the polymer was isolated on a frit washing well with methanol. The products were then purified by passage through a silica gel column (1 in. diameter × 3 in. length) eluting with $CHCl_3$. Concentration of the appropriate fractions yielded a white solid.

E. General Procedure for Polymerization of Isobutylene Using Complexes 3a and 3b. A Schlenk flask containing a stir-bar was cooled to −78 °C under a nitrogen atmosphere. Isobutylene (1.5−2 mL) was condensed into the flask followed by slow addition of 3 mL of CH_2Cl_2 via syringe. A second Schlenk flask containing a solution of either **3a** or **3b** (5.5 μmol) in 1 mL of CH_2Cl_2 was cannula transferred into the flask containing the isobutylene and followed by washing with an additional 0.5 mL of CH_2Cl_2. The reaction mixture was stirred at −78 °C for 15 min and then at 0 °C in an ice bath for 10 min. The ice bath was removed, and the reaction mixture was stirred for an additional 1 h at room temperature. The reaction mixture was then quenched with MeOH, and the volatiles were removed in vacuo on a rotary evaporator leaving an oil. The oil was dissolved in hexanes and filtered to remove the iridium-containing species. Removal of the hexanes in vacuo yielded approximately 1.5 g of a colorless, viscous oil whose ^{1}H NMR spectrum matched that reported in the literature.[44]

F. General Procedure for Oligomerization of Norbornene Using Complexes 3a and 3b. A 25 mL round-bottom flask containing a stir-bar was charged with 6 mL of CH_2Cl_2 and norbornene (120 mg, 1.3 mmol, 118 equiv). Either **3a** or **3b** (11 μmol) was then added to the solution as a solid. The reaction mixture was stirred at room temperature for 2 days before quenching with MeOH. After solvent evaporation, the resulting oil was dissolved in $CHCl_3$ and passed through a silica gel column (1 in. diameter × 3 in. length). Concentration of the first yellow fraction off the column yielded approximately 110 mg of a yellow oil whose ^{1}H NMR spectrum matched that reported in the literature.[42]

G. General Procedure for Oligomerization of α-Methylstyrene Using 3a or 3b. The reaction was conducted in an NMR tube, and the products were characterized spectroscopically. No material was isolated from the reaction. A resealable NMR tube was charged with **3a** or **3b** (5.7 μmol) and 0.5 mL of CD_2Cl_2. α-Methylstyrene (285 μmol, 50 equiv) was then added via syringe resulting in an exothermic reaction. After 5 min, a ^{1}H NMR spectrum was obtained and confirmed complete conversion of the monomer into a 1:1 (dimer:trimer) mixture whose ^{1}H NMR spectrum matched that reported in the literature.[2]

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Supporting Information Available: Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org..

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