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New Cationic Iridium(III) Complexes of Diiodobenzene as Electrophilic Catalysts: Using Chelation and Lability in Concert

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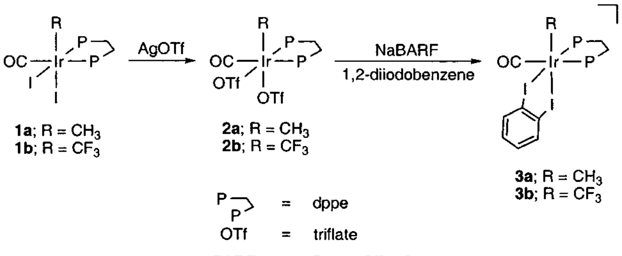
Cationic complexes of the platinum group elements that are soluble in less polar, aprotic media represent fertile targets for the synthesis and development of electrophilically driven systems for catalysis and bond activation. Notable achievements in this regard include $PdMe(sol)(L-L)^+$, where L−L = diimine or di(phosphine) and sol = coordinated solvent for $CO + C_2H_4$ copolymerization,[1,2] related $PdMe(sol)(Ar_2DAB)^+$ systems, where Ar_2DAB = diaryldiazabutadiene for ethylene and α-olefin polymerization,[3−5] and $PtMe(sol)(NN)^+$ complexes, where NN = Me_4en or Ar_2DAB for C−H bond activation.[6−9] All of these complexes have weakly bound solvent molecules as ligands and essentially noncoordinating anions such as $B(3,5-(CF_3)_2C_6H_3)_4^-$ or $BARF^-$. As a d^6 metal ion, Ir(III) is thought to possess the electrophilic character of Pd^{2+} but its configuration in a hexacoordinate environment confers inertness on its cationic complexes. The ability to overcome this inertness has been demonstrated by $(Cp^*)IrMe(PMe_3)(CH_2Cl_2)^+$, which in the presence of $^{13}CH_4$ gives evidence of facile loss of weakly bound CH_2Cl_2, C−H bond activation, and methane exchange.[10] In studies designed to generate Ir(III) complexes having adjacent labile sites, we have previously reported[11] the synthesis of the bis(triflate) complex $IrMe(CO)(dppe)(OTf)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane, OTf = triflate), which is a weak electrolyte in dichloromethane, and the dicationic acetyl complex $Ir(C(O)Me)(dppe)(MeCN)_3^{2+}$ as its PF_6^- salt. In their reaction chemistry, both of these complexes show evidence of facile ligand dissociation that leads to electrophilic behavior. In this report, we describe two new Ir(III) cations that exhibit greatly enhanced electrophilic reactivity, including the initiation of a variety of cationic polymerizations. The complexes are rendered stable enough for isolation and characterization by use of the labile chelating ligand 1,2-diiodobenzene (DIB), which was first observed to function in this way by Crabtree in 1982.[12]

Scheme 1



1a; R = CH_3
1b; R = CF_3

2a; R = CH_3
2b; R = CF_3

3a; R = CH_3
3b; R = CF_3

P P = dppe
OTf = triflate
BARF = $B(3,5-(CF_3)_2C_6H_3)_4^-$

Synthesis of the DIB adducts **3a** and **3b** (Scheme 1) can be accomplished in two steps starting from the Ir(III) diiodide complexes $IrR(CO)(dppe)I_2$, where R = CH_3 (**1a**) and CF_3 (**1b**). As found for **1a**,[11] halide abstraction from **lb** with 2 equiv of AgOTf in CH_2Cl_2 generates $Ir(CF_3)(CO)(dppe)(OTf)_2$ (**2b**). 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 excess DIB, formation of a single Ir species[13] is observed. After filtration of the NaOTf precipitate and subsequent solvent evaporation, thermally stable white solids are obtained from the reactions. Complexes **3a** and **3b** demonstrate clean spectroscopic features in their ^{31}P, ^{19}F, and ^1H NMR spectra.[14] Complete metathesis of the OTf^- ions from **3** is evidenced by the absence of triflate resonances in the ^{19}F NMR spectrum and by the presence of that for the CF_3 groups of the BARF anion at 0.24 ppm. Likewise, 1:1 resonances in the ^{31}P NMR spectra of **3a** and **3b** indicate that the complexes each have two different ^{31}P environments resulting from different ligands trans to the dppe phosphine donors.[15] Although the coordinated DIB resonances are partially masked by the dppe phenyl groups, dissolution of the complexes in CD_3CN results in rapid conversion to the corresponding bis acetonitrile complexes[16] **4a** and **4b** with concomitant liberation of 1 equiv of DIB.

A closer investigation of the MeCN exchange reaction at low temperatures indicates that DIB displacement occurs in two steps for both of the complexes. For **3a**, the initial exchange begins at −40 °C, approximately 15 °C lower than that for complex **3b**. Additionally, reactions with ^{13}CO as the incoming ligand verify that the first exchange occurs trans to the alkyl group followed by equatorial exchange resulting in formation of the tricarbonyl complex $IrR(CO)_3(dppe)^{2+}$ and free DIB.[17] For both **3a** and **3b**, the reactions with CO and MeCN appear to proceed via the same pathway as evidenced by similar chemical shifts in the ^{31}P NMR spectra of the intermediate species. Facile substitution of DIB by simple carboxylate esters further supports the notion of the lability of **3**. Two equivalents of methyl acetate displace DIB from **3a** irreversibly to generate $IrCH_3(CO)(dppe)(CH_3COOCH_3)_2^{2+}$ in situ, whereas methyl acrylate yields an equilibrium mixture of the ester disubstitution product and the starting complex. There is no evidence, however, of interaction between **3a** and the olefinic bond of methyl acrylate. Complex **3a** does not show evidence of

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(13) For complex **3a**, longer reaction times result in increased formation of a symmetrical product arising from isomerization of **3a**, $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.20 (s).

(14) Complex **3a**: ^1H NMR (CD_2Cl_2) δ 7.02−7.83 (overlapping, 48H, phenyl, DIB, BARF), 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, $Ir-CH_3$); $^{31}P\{^1H\}$ 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, Cl_2) δ 0.24 (s, BARF). Complex **3b**: ^1H NMR (CD_2Cl_2) δ 6.86−7.93 (overlapping, 48H, phenyl, DIB, BARF), 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).

(15) An unsymmetrical orientation of CO relative to dppe is also supported by the J_{P-C} cis (*ca.* 6 Hz) and trans (*ca.* 120 Hz) magnitudes. See: Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714−721.

(16) Generation of **4a**,**b** may also be accomplished by reacting **2a**,**b** which thus NaBARF in the presence of MeCN and supports the assignments.

(17) Conversion of methyl complex **3a** to the corresponding tricarbonyl is complete. However, the CF_3 analogue **3b** yields only ca. 10% (by NMR) of the tricarbonyl species with the remainder decomposing over time into numerous unidentified species.

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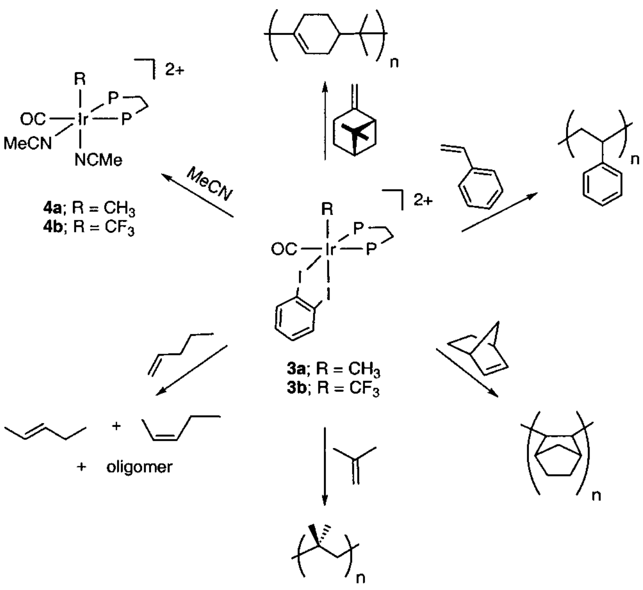
Scheme 2



reaction with stoichiometric amounts of ethylene, but does exhibit reaction when the latter is present in large excess, leading to the formation of a fluxional complex having equivalent phosphines and ethylene ligands at 298 K. However, no evidence of polymerization or oligomerization is seen. With l-pentene as the olefin, double bond isomerization occurs over the period of several days at room temperature to yield *cis*- and *trans*-2-pentene, as determined spectroscopically and by GC analysis. The reaction leads to a product distribution of 2% 1-pentene, 14% *cis*-2-pentene, and 84% *trans*-2-pentene that is slightly enriched in the trans isomer relative to the thermodynamic ratio under these conditions.[18] During the isomerization, complex **3a** is observed as the only organometallic species in solution. When the same reaction is repeated in the presence of ethylene (olefin ratio ≈ 1:1), retardation of isomerization is seen indicating that ethylene and 1-pentene coordinations are competitive. The mechanism most likely proceeds via olefin binding to Ir(III) followed by allylic proton dissociation and subsequent reprotonation to give the isomerized olefin. The fact that oligomerized olefin[19] is also observed in trace amounts from the reaction suggests that **3a** has the ability to generate a secondary carbocation with 1-pentene, a notion supported by the polymerization reactions discussed below.

The most notable evidence of electrophilic reactivity of **3** is given by polymerizations the complexes are found to promote (Scheme 2). For isobutylene, β-pinene, and styrene,[20] addition of the respective olefin to dichloromethane solutions of the DIB complexes results in exothermic reactions where the monomers are rapidly consumed and the solvent begins to boil. Analysis of the solutions demonstrates conversion of the monomers to polymerized/oligomerized olefin in all cases.[21] Polystyrene and poly-β-pinene products are isolated as solids, whereas polyisobutylene polymerizations yield viscous oils. For norbornene as the olefin, polymerization occurs more slowly 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[22,23] are not occurring. Furthermore, the complexity of a H,H-COSY of the isolated oligomer suggests that both 2,3- (Scheme 2) and 2,7-additions are happening due to norbornyl cation formation (vide infra).

The fact that **3a** does not actively polymerize ethylene whereas both **3a** and **3b** promote polymerization of isobutylene, norbornene, styrene, and β-pinene suggests that polymerization proceeds via a cationic mechanism with **3** serving as the initiator rather than by a coordination/insertion mechanism. The wide range of observed polydispersities supports this notion. Furthermore, quenching of styrene polymerization with *tert*-butyl alcohol 5 s after monomer addition to a CH_2Cl_2 solution of **3a** results in incorporation of a *tert*-butyl ether end group into the polymer chain, as seen by a large singlet at δ 1.26 in the ^{1}H NMR spectrum. Since initiation by the metal complex can occur by either direct reaction with the olefin or indirect reaction with trace water to generate H^+, definitive evidence supporting either pathway under *normal* reaction conditions cannot be offered. However, metal complex end groups[24] in chromatographed poly-β-pinene and polystyrene have been detected by ^{31}P NMR spectroscopy for reactions conducted in the presence of the hindered base 2,6-di-*tert*-butylpyridine (>4 equiv xs). Although monomer consumption is expectedly slower when base is present, consumption of the metal complex is observed indicating that direct initiation is occurring. While cationic promotion and polymerization by metal complexes has been seen previously for a few late metal complexes,[25] the reactivity reported here for DIB complexes **3a** and **3b** is unprecedented for Ir(III) systems. Further work examining the reaction chemistry of these complexes is in progress.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Similar reactions conducted with α-methylstyrene result in indan formation supporting cationic initiation by **3**. See ref 25 for more details.

[21] Polystyrene: [**3a**, $M_w = 22\,200$, PDI = 5.9] and [**3b**, $M_w = 23\,800$, PDI = 4.9]. Poly-β-pinene: [**3a**, $M_w = 21\,900$, PDI = 2.5] and [**3b**, $M_w = 12\,900$, PDI = 2.91]. Polyisobutylene: [**3a**, $M_w = 1940$, PDI = 2.6] and [**3b**, $M_w = 3430$, PDI = 3.8]. Polynorbornylene: [**3a**, $M_w = 234$, PDI = 1.2] and [**3b**, $M_w = 262$, PDI = 1.2].

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[24] ^{31}P NMR spectra for poly-β-pinene (3 h) and for polystyrene (>12 h) revealed resonances of phosphine donors; for PS, two broad resonances around 11 ppm were seen, one of which had coupling to ^{13}C using carbonyl-labeled **3a**.

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