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Lewis Acids and Lewis Acid-Functionalized Ligands in Rhodium-Catalyzed Methyl Acetate Carbonylation

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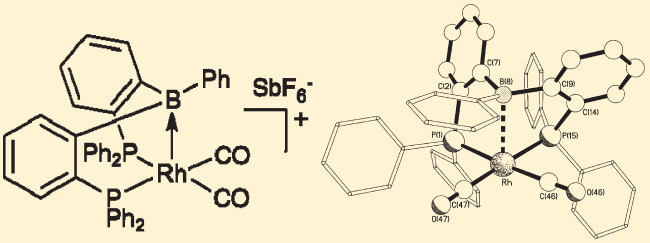
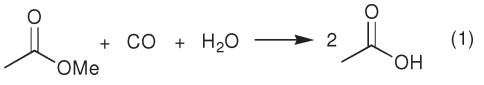
Supporting Information

ABSTRACT: The application of Lewis acids and Lewis acid-functionalized ligands as activators for methyl acetate in the rhodium-catalyzed carbonylation of methyl acetate to acetic anhydride has been investigated. The reaction of methyl acetate with $B(C_6F_5)_3$ results in the formation of the adduct $[MeOAc\cdot B(C_6F_5)_3]$. The combination of this adduct with $[Rh(OAc)(CO)_2]_2$ results in a transfer of the Lewis acid to the rhodium complex, rather than an anticipated oxidative addition reaction. In a second approach, novel Lewis acid-functionalized rhodium(I) complexes $[Rh(CO)Cl(BPP)]$, $[Rh(CO)_2(BPP)]SbF_6$, and $[Rh(MeCN)_2(BPP)]SbF_6$ (BPP = $PhB(C_6H_4PPh_2)_2$) have been prepared. The lack of reactivity of $[Rh(CO)_2(BPP)]SbF_6$ toward MeOAc has shown that the rhodium−boron interaction is too strong for activation of methyl acetate, and no carbonylation activity was observed under the conditions used.



INTRODUCTION

The carbonylation of methanol and methyl acetate are currently the most important industrial processes for the large-scale production of acetic acid and acetic anhydride.[1−3] Annual production capacity is seven million tonnes worldwide and continues to grow, especially in Asia.[4] The catalyst system for these carbonylation reactions typically comprises a rhodium or iridium source and an iodide cocatalyst. Acetic acid is used as the solvent and, under the reaction conditions, methanol is rapidly converted to methyl acetate, which therefore constitutes the actual substrate. Because OAc^- forms a better leaving group than OH^- in the pivotal C−O bond cleavage reaction, methyl acetate reacts initially with iodide to form methyl iodide, which is subsequently carbonylated and eventually hydrolyzed to acetic acid, according to the overall reaction in eq 1. In the absence of water, methyl acetate is carbonylated to acetic anhydride.



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The high temperatures and strongly acidic reaction conditions required for carbonylation reactions, combined with the use of iodide as the cocatalyst, present significant challenges in terms of reactor engineering and corrosion prevention. Alternative catalysts that can be used under milder reaction conditions and avoid the use of iodide could significantly lower the cost of acetic acid and acetic anhydride production. Several alternative strategies for the activation of methanol have been investigated, for example the application of solid acids, such as zeolites,[5−8] and heteropolyacids[9] or superacids.[10] These strong acids can protonate methanol, which upon elimination of H_2O generates a carbenium cation, CH_3^+.[8,10] Although these strong acids can carbonylate methanol without the presence of iodide, the selectivities are generally lower due to the formation of significant amounts of dimethyl ether.[9,11,12]

An alternative approach would be to use Lewis acids for the activation of methyl acetate. Lewis acids are known to be able to activate C−O bonds in a variety of organic and inorganic transformations as well as in catalysis.[13−19] For example, in carbocationic olefin polymerization, BCl_3 is used to activate alkylacetate esters to generate $[BCl_3(OAc)]^-$ and a carbenium cation, which initiates the polymerization reaction.[20] It is also known that esters, for example, ethyl acetate, bind reversibly via the carbonyl oxygen atom to Lewis acids such as $B(C_6F_5)_3$ to form an adduct, $[EtOAc\cdot B(C_6F_5)_3]$.[21] These findings suggest that Lewis acids might be applicable in place of Brønsted acids for the C−O bond activation and carbonylation of methyl acetate, according to the reaction scheme depicted in Scheme 1. The anion $[B(C_6F_5)_3(OAc)]^-$ has been reported previously.[22]

Here we have investigated the application of Lewis acids and Lewis-acid-functionalized ligands in the catalytic carbonylation of methyl acetate. The first part of this study describes our investigations into the application of *external* Lewis acids such as

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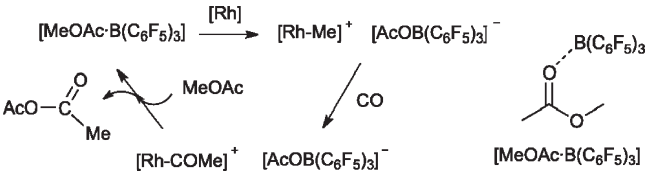
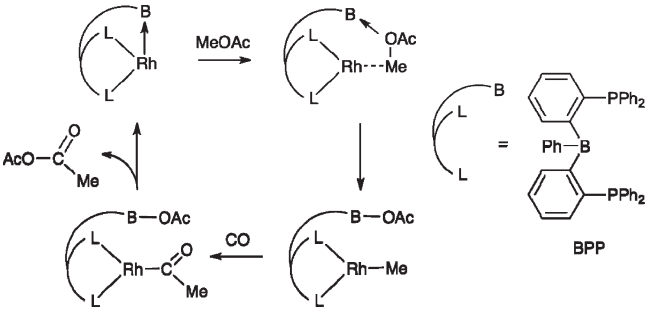
Scheme 1



Scheme 2



$B(C_6F_5)_3$ in the activation and carbonylation of methyl acetate. In the second part of this study, we have investigated the application of metal complexes with a ligand that contains an *internal* Lewis acid. The coordination chemistry of ligands with Brønsted acidic or basic functionalities and their application in homogeneous catalysis has been an ongoing theme in our laboratory, and we have previously reported on the use of such ligands in the context of alkane oxidation[23−25] and for methyl acetate carbonylation.[26] Our attention was drawn to the interesting transition metal complexes developed by Bourissou and co-workers, which contain diphosphine ligands of the type $PhB(C_6H_4PR_2)_2$ (R = ^{i}Pr, Ph) with a Lewis acidic boron center.[27−29] These ambiphilic phosphonyl borane ligands coordinate to the metal center through the phosphine donors and the Lewis acidic boron center. Metal-boron interactions of this type are relatively new and are attracting considerable attention.[30] Of particular interest to this study are the observations by Parkin and co-workers that certain nickel and iron complexes, containing ligands with a dative covalent metal−boron interaction, can activate carbon−halide bonds to yield complexes with halide anions bound to the boron center.[31,32] We were intrigued whether this activation strategy could also be applied to methyl acetate activation and carbonylation, as depicted schematically in Scheme 2.

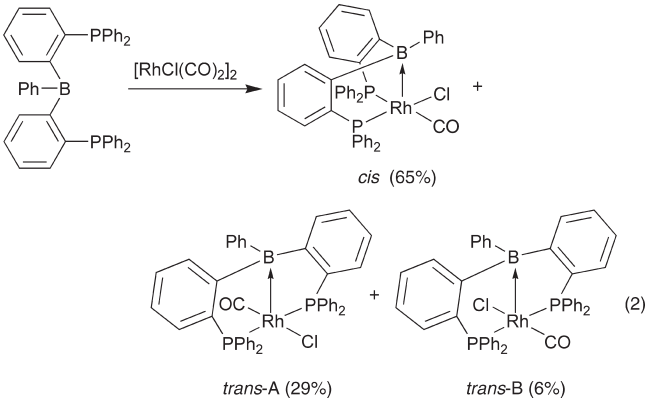
Here we present the synthesis of the adduct $[MeOAc\cdot B(C_6F_5)_3]$ and its reactivity toward $[Rh(OAc)(CO)_2]_2$ in an attempt to activate methyl acetate using the *external* Lewis acid $B(C_6F_5)_3$. In addition, the synthesis and characterization of new rhodium(I) complexes containing the diphosphanyl borane ligand $PhB(C_6H_4PPh_2)_2$ is reported. These complexes contain an *internal* Lewis acid functionality, and an investigation into their application in C−O bond activation and carbonylation catalysis has been carried out. The formation of a boron−MeOAc adduct is a common feature in both strategies, in an attempt to achieve the essential O−Me oxidative addition reaction at the rhodium center.

RESULTS AND DISCUSSION

Synthesis of Ligands and Complexes. $B(C_6F_5)_3$ was reacted with an excess of methyl acetate in pentane to yield the novel adduct $[MeOAc\cdot B(C_6F_5)_3]$, which was characterized by multinuclear NMR spectroscopy, elemental analysis, and IR spectroscopy. The ν(C=O) and ν(B−O) bands are observed at 1649 and 1469 cm^{-1}, which are very similar to the values reported for $[EtOAc\cdot B(C_6F_5)_3]$.[21]

The ligand $PhB(C_6H_4PPh_2)_2$ (BPP) was previously described by Bourissou and co-workers.[33] We used a slightly different procedure for the synthesis of BPP. A palladium coupling reaction between 1,2-iodobromobenzene and $HPPh_2$ in toluene resulted in *o*-bromophenyl diphenylphosphine,[34] which was lithiated with ^{n}BuLi according to the procedure described by Harder et al.[35] Half an equivalent of $PhBCl_2$ was reacted with the lithium compound in toluene to yield the diphosphanyl borane ligand BPP as a white solid in 52% yield.

$[RhCl(CO)_2]_2$ was reacted with two equivalents of BPP in dichloromethane to obtain [Rh(CO)Cl(BPP)] as a yellow solid in 65% yield. Elemental analysis and LSIMS mass spectrometry confirm the composition of [Rh(CO)Cl(BPP)], but ^{31}P NMR spectroscopy (Figure 1) shows that three separate isomers exist in solution, which are assigned as *cis*, *trans*-A, and *trans*-B (see eq 2). The ^{31}P NMR spectrum displays two doublets centered at 28.4 and 33.8 ppm with $^1J_{P-Rh}$ coupling constants of 110.1 and 106.3 Hz, which are tentatively assigned to the *trans*-B and *trans*-A complexes, respectively. In the case of a similar rhodium diphosphanyl borane complex, [Rh(DPB)(CO)Cl] (DPB = $PhB(C_6H_4P^iPr_2)_2$), DFT calculations have suggested that the major *trans*-isomer has the phenyl group orientated above the carbonyl ligand (like *trans*-A).[28] The *cis*-isomer of [RhCl(CO)(BPP)] is observed in the ^{31}P NMR spectrum as two double doublets at 54.2 and 36.3 ppm, with $^1J_{P-Rh}$ coupling constants that equal 146.1 and 119.2 Hz, respectively, and a $^2J_{P-P}$ value of 36.4 Hz. At 298 K in $CDCl_3$, the *cis*-isomer of [RhCl(CO)(BPP)] accounts for 65% of all the species in solution, *trans*-A 29%, and *trans*-B 6%. ^{31}P NMR spectra in $CDCl_3$ at 223 and 323 K did not show any changes, indicating that there is no equilibrium between these isomers.



One equivalent of $AgSbF_6$ was reacted with [RhCl(CO)(BPP)] in chloroform under a CO atmosphere to yield $[Rh(CO)_2(BPP)]SbF_6$, which was isolated as a yellow solid in 61% yield (eq 3). Only one isomer is observed in the

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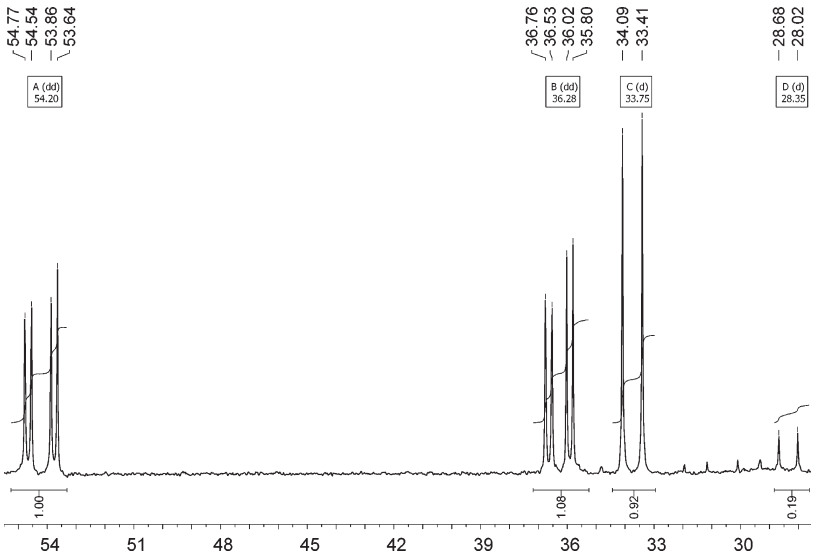
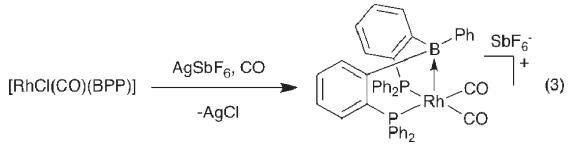
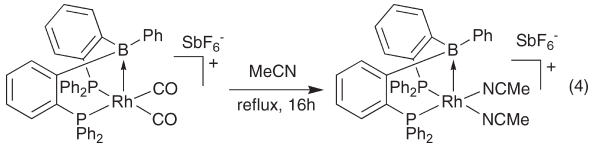


Figure 1. ^{31}P NMR spectrum of [RhCl(CO)(BPP)] in $CDCl_3$ at 298 K.

^{31}P NMR spectrum. A doublet at 35.5 ppm with a $^{1}J_{P-Rh}$ coupling constant of 119.3 Hz indicates that the phosphine donors are in *cis*-conformation. Two ν(CO) bands in the IR spectrum at 2123 and 2096 cm^{-1} confirm a dicarbonyl complex, as does the double doublet in the ^{13}C NMR spectrum at 178.7 ppm. The $^{1}J_{C-Rh}$ and $^{2}J_{C-P}$ coupling constants are very similar and cannot be distinguished. The parent ion peak $[M]^+$ is observed in the positive ESI mass spectrum at 769 *m*/*z*, and the SbF_6^- counterion is identified in the negative ESI mass spectrum at 235 *m*/*z*. A singlet is observed in the ^{11}B NMR spectrum at 0.45 ppm, shifted upfield from 29.6 ppm for [RhCl(CO)(BPP)].





An unusual spectroscopic feature of this complex is the absence of any fluorine signals in the ^{19}F NMR spectrum in benzene, chloroform, and dichloromethane at room temperature. At this stage we can only speculate that given the fluorophilicity of the boron center,[36] this spectroscopic phenomenon is caused by interactions of the SbF_6^- anion with the quadrupolar boron center. The ^{19}F NMR spectra at 233 and 323 K of $[Rh(CO)_2(BPP)]SbF_6$ did not show any changes compared to the spectrum at 298 K.

When $[Rh(CO)_2(BPP)]SbF_6$ was dissolved in d_3-acetonitrile, a reaction took place converting $[Rh(CO)_2(BPP)]SbF_6$ partially (~90%) to $[Rh(d_3\text{-MeCN})_2(BPP)]SbF_6$. For this complex the SbF_6^- anion is observed in the ^{19}F NMR spectrum. The reaction

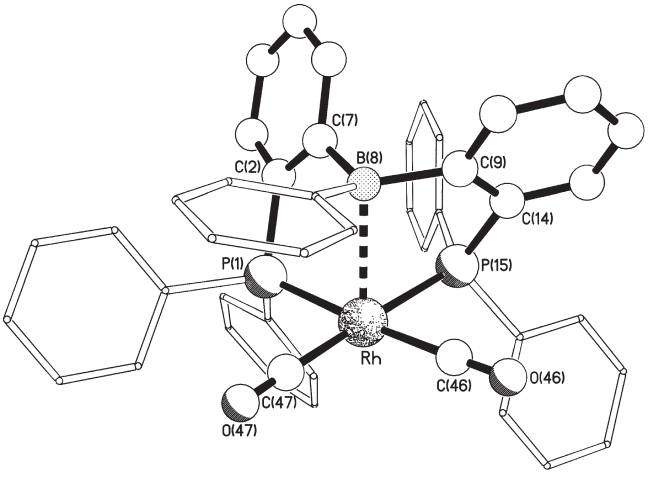


Figure 2. Molecular structure of $[Rh(CO)_2(BPP)]^+$. Selected bond lengths (Å) and angles (deg): Rh−P(1), 2.3116(6), Rh−P(15), 2.3604(6), Rh···B(8), 2.449(3), Rh−C(46), 1.958(3), Rh−C(47), 1.950(3), P(1)−Rh−B(8), 83.04(7), P(1)−Rh−P(15), 93.43(2), B(8)−Rh−P(15), 78.64(6), C(46)−Rh−C(47), 90.18(11).

was repeated by stirring $[Rh(CO)_2(BPP)]SbF_6$ in nondeuterated acetonitrile at room temperature for 16 h (eq 4), and the product $[Rh(MeCN)_2(BPP)]SbF_6$ was fully characterized by multinuclear NMR spectroscopy, X-ray diffraction analysis, mass spectrometry, elemental analysis, and IR spectroscopy. Dissolution of $[Rh(MeCN)_2(BPP)]SbF_6$ in $CDCl_3$ allows comparison of the NMR spectra with those of $[Rh(CO)_2(BPP)]SbF_6$. The phosphine donor signal in the ^{31}P NMR spectrum resonates at 54.3 ppm, with a $^{1}J_{P-Rh}$ of 155.5 Hz, which is ~19 ppm downfield relative to the signal of $[Rh(CO)_2(BPP)]SbF_6$. The fluorine signal of SbF_6^- is present at −123 ppm in the ^{19}F NMR spectrum, and a broad singlet at 8.1 ppm is observed in the ^{11}B NMR spectrum, slightly downfield from the boron signal of $[Rh(CO)_2(BPP)]SbF_6$, which is at −0.5 ppm.

Solid-State Structures. Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane

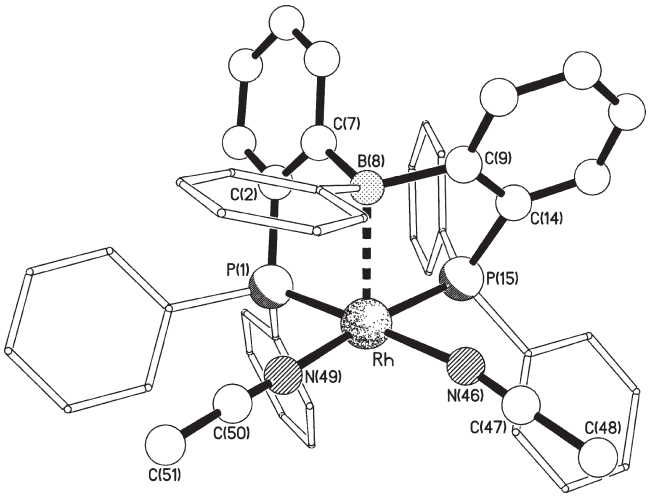


Figure 3. Molecular structure of $[Rh(MeCN)_2(BPP)]^+$. Selected bond lengths (Å) and angles (deg): Rh−P(1), 2.2298(7), Rh−P(15), 2.2631(7), Rh···B(8), 2.288(3), Rh−N(46), 2.104(3), Rh−N(49), 2.099(3), P(1)−Rh−B(8), 84.02(9), P(1)−Rh−P(15), 93.50(3), B(8)−Rh−P(15), 80.36(9), N(46)−Rh−N(49), 87.07(11).

into dichloromethane solutions of $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$. The structures of $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$ with selected bond lengths and angles are shown in Figures 2 and 3, respectively. For comparison, the rhodium diphosphanyl borane complex *trans*-[RhCl(CO)(DPB)] ((DPB = $PhB(C_6H_4P^iPr_2)_2$), which was previously reported by Bourissou and co-workers, has Rh−P bond lengths of 2.332(1) and 2.327(1) Å and a Rh−B bond length of 2.374(3) Å.[28]

The rhodium center in both $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$ adopts a square-based pyramidal coordination geometry with a *fac* conformation for the BPP ligand (see Figures 2 and 3 respectively). This contrasts with the structure of [RhCl(CO)(DPB)], which, while also having a square-based pyramidal coordination geometry, has a *mer* conformation for the closely related DPB ligand.[28] The boron center occupies the apical site, but the potential C_s symmetry is broken in each case by a twist about the Rh···B vector such that the boron-bound phenyl ring sits above one of the carbonyl/acetonitrile ligands; the associated C_{Ph}−B(8)−Rh−C(47)/N(49) dihedral angles are 11° and 12° in $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$, respectively. This places the centroid of the aryl ring approximately 3.20 and 3.22 Å from the centroid of the C≡O and N≡C triple bonds, respectively. The Rh−P bond lengths are asymmetric, with those to P(15) being longer than those to P(1) by 0.05 and 0.03 Å in $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$, respectively (see Figures 2 and 3, respectively). This asymmetry is presumably associated with the twisting of the BPP ligand discussed above; the longer Rh−P bonds are those *trans* to the carbonyl/acetonitrile ligand proximal to the boron-bound aryl ring.

Carbon monoxide is a stronger π-acceptor ligand than acetonitrile. Consequently, changing the CO ligands in $[Rh(CO)_2(BPP)]SbF_6$ for MeCN ligands (eq 4) results in an increase of electron density at the metal center, which in turn results in contractions of the Rh−P and Rh···B distances by 0.08, 0.10, and 0.21 Å for the Rh−P(1), Rh−P(15), and Rh−B(8) bonds, respectively. The shortening of the Rh···B bond is particularly interesting, as it suggests that the strength of the rhodium−boron interaction can be tuned by modifying the metal-bound ligands. A relatively weak Rh···B interaction would be desirable for substrate activation, as shown in Scheme 2.

Oxidative Addition Reactions. The oxidative addition of methyl iodide at the rhodium(I) center of $[RhI_2(CO)_2]^-$ is an essential and rate-determining step in the carbonylation of methanol.[1] Methyl acetate does not react directly with rhodium(I) complexes such as $[RhI_2(CO)_2]^-$, and therefore iodide is required for the initial conversion of methyl acetate into methyl iodide, which subsequently reacts with the rhodium complex. In order to assess whether boranes such as $B(C_6F_5)_3$ could be used to activate methyl acetate for the oxidative addition at rhodium(I) complexes, we have investigated the reaction between $[MeOAc\cdot B(C_6F_5)_3]$ and $[Rh(OAc)(CO)_2]_2$. This particular rhodium complex was chosen instead of $[RhI_2(CO)_2]^-$ to avoid halide exchange reactions and the formation of methyl iodide.

The reaction of two equivalents of $[MeOAc\cdot B(C_6F_5)_3]$ with one equivalent of the dimeric complex $[Rh(OAc)(CO)_2]_2$ in C_6D_6 was monitored by ^1H NMR spectroscopy (see spectrum 3 in Figure 4). The two methyl signals at 1.07 and 3.02 ppm for $[MeOAc\cdot B(C_6F_5)_3]$ shift to 1.61 and 3.28 ppm, which are the signals for methyl acetate in C_6D_6. The methyl signal of $[Rh(OAc)(CO)_2]_2$ is shifted from 1.68 ppm to 1.34 ppm. Analysis of the ^{19}F and ^1H NMR spectroscopic data discounts the formation of the elimination product $[(AcO)B(C_6F_5)_3]^-$, which is a known anion,[22] and no ^1H NMR signals corresponding to the products of a methyl acetate oxidative addition reaction are observed. The reaction of $[Rh(OAc)(CO)_2]_2$ with two equivalents of $B(C_6F_5)_3$ results in a new complex with a single methyl resonance at 1.34 ppm (see spectrum 5 in Figure 4). It appears that the Lewis acid $B(C_6F_5)_3$ binds more strongly to the rhodium complex $[Rh(OAc)(CO)_2]_2$ than to methyl acetate, resulting in a new complex, $[Rh(OAc)(CO)_2\cdot B(C_6F_5)_3]$, of an as yet unknown structure.

$B(C_6F_5)_3$ could form an adduct with $[Rh(OAc)(CO)_2]_2$ either by binding directly to the rhodium center or by binding to the oxygen atoms of the carbonyl or the acetate ligands. The coordination of Lewis acids to terminal CO ligands in metal carbonyl complexes is well known,[37−40] including examples of $B(C_6F_5)_3$ binding to the carbonyl ligands in iron(II) and ruthenium(II) complexes.[41] From the stoichiometry of the reaction, it appears that two equivalents of $B(C_6F_5)_3$ bind to a single equivalent of $[Rh(OAc)(CO)_2]_2$ to form a new product. Several attempts to isolate the product $[Rh(OAc)(CO)_2\cdot B(C_6F_5)_3]$ invariably resulted in decomposition.

Oxidative addition reactions of complex $[Rh(CO)_2(BPP)]SbF_6$ were carried out with methyl acetate and trifluoromethyl acetate. The complex was dissolved in separate solutions of trifluoromethyl acetate and methyl acetate in $CDCl_3$ (4 M) and heated to 70 °C. The reactions were monitored by ^1H and ^{31}P NMR spectroscopy over the course of seven days. No rhodium-bound methyl or acetyl signals were observed. The only methyl signals observed were those of trifluoromethyl acetate and methyl acetate, suggesting that the rhodium−boron bond was not cleaved to yield a boron methyl acetate or boron trifluoromethyl acetate adduct as anticipated in Scheme 2.

The oxidative addition of methyl iodide to $[Rh(CO)_2(BPP)]SbF_6$ was also investigated. $[Rh(CO)_2(BPP)]SbF_6$ was dissolved in a solution of methyl iodide in $CDCl_3$ (4 M), and the reaction

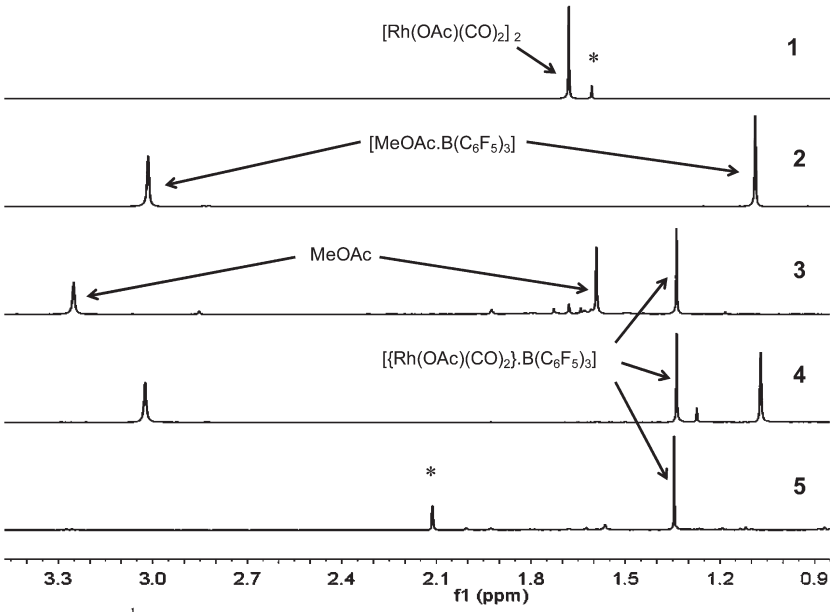


Figure 4. ^{1}H NMR spectra monitoring a series of reactions between $[Rh(OAc)(CO)_2]_2$, $B(C_6F_5)_3$, and $[MeOAc\cdot B(C_6F_5)_3]$ in C_6D_6 at 298 K. Spectrum 1: $[Rh(OAc)(CO)_2]_2$; spectrum 2: $[MeOAc\cdot B(C_6F_5)_3]$; spectrum 3: $[Rh(OAc)(CO)_2]_2 + 2\ [MeOAc\cdot B(C_6F_5)_3] \rightarrow 2\ [Rh(OAc)(CO)_2\cdot B(C_6F_5)_3] + 2$ MeOAc; spectrum 4: $[Rh(OAc)(CO)_2]_2 + 2\ [MeOAc\cdot B(C_6F_5)_3] + 2\ B(C_6F_5)_3 \rightarrow 2\ [Rh(OAc)(CO)_2\cdot B(C_6F_5)_3] + 2\ [MeOAc\cdot B(C_6F_5)_3]$; spectrum 5: $[Rh(OAc)(CO)_2]_2 + 2\ B(C_6F_5)_3 \rightarrow 2\ [Rh(OAc)(CO)_2\cdot B(C_6F_5)_3]$. * = impurities: NaOAc in spectrum 1 and $[B(C_6F_5)_3\cdot H_2O]$ in spectrum 5.

was monitored by ^{1}H and ^{31}P NMR spectroscopy at room temperature over seven days. The reaction resulted in multiple unknown products, but no rhodium-bound methyl or acetyl species were observed.

Carbonylation Experiments. A series of carbonylation experiments were carried out under anhydrous conditions without an iodide cocatalyst. A mixture of $[MeOAc\cdot B(C_6F_5)_3]$ and $[Rh(OAc)(CO)_2]_2$ (10:1) was dissolved in dry methyl acetate and transferred into a nitrogen-purged high-pressure reactor. The reactor was charged with 40 bar of CO and heated for 16 h at 150 °C and at 200 °C. No methyl acetate carbonylation was observed in any of these experiments. In another experiment, $[Rh(CO)_2(BPP)]SbF_6$ was reacted in methyl acetate at 130 °C under 40 bar of CO pressure for 16 h. No methyl acetate carbonylation products could be detected.

CONCLUSIONS

The aim in this study was to use Lewis-acidic triaryl boron compounds to weaken or cleave the O−Me bond in methyl acetate in order to form rhodium−methyl complexes via an oxidative addition reaction, with a view to carbonylating methyl acetate to acetic anhydride. The reaction between $[MeOAc\cdot B(C_6F_5)_3]$ and $[Rh(OAc)(CO)_2]_2$ did not yield an oxidative addition product but instead resulted in the transfer of the Lewis acid from methyl acetate to the rhodium complex, resulting in a new adduct, $[Rh(OAc)(CO)_2\cdot B(C_6F_5)_3]$, which could not be isolated or structurally characterized.

In a second part of this study, a series of novel Lewis acid-functionalized rhodium complexes $[Rh(CO)Cl(BPP)]$, $[Rh(CO)_2(BPP)]SbF_6$, and $[Rh(MeCN)_2(BPP)]SbF_6$ were synthesized and fully characterized. The carbonyl ligands of $[Rh(CO)_2(BPP)]SbF_6$ were substituted for MeCN ligands in quantitative yield upon reaction of $[Rh(CO)_2(BPP)]SbF_6$ with acetonitrile. Reactions of $[Rh(CO)_2(BPP)]SbF_6$ with methyl acetate and acetonitrile demonstrated that the rhodium−boron bond in $[Rh(CO)_2(BPP)]SbF_6$ is too strong for cleavage to occur. An interesting feature observed in the molecular structures of $[Rh(CO)_2(BPP)]SbF_6$ and $[Rh(MeCN)_2(BPP)]SbF_6$ is a shortening of the Rh−B bond upon substituting the carbonyl ligands for acetonitrile ligands, which suggests that the rhodium−boron interaction can be "tuned" by ligand alterations. The application of Lewis acid-functionalized complexes with weaker metal−boron interactions should be more effective in carbonylation catalysis, and these will be investigated next.

EXPERIMENTAL SECTION

General Procedures. All moisture- and oxygen-sensitive compounds were prepared using standard high vacuum line, Schlenk, and cannula techniques. A standard nitrogen-filled glovebox was used for any subsequent manipulation and storage of these compounds. Standard ^{1}H, ^{19}F, ^{31}P, ^{11}B, and ^{13}C NMR spectra were recorded using a Bruker AV400 spectrometer. ^{1}H NMR chemical shifts were referenced to the residual nondeuterated solvent signal; ^{13}C NMR chemical shifts, to the signal of the deuterated solvent. The ^{31}P NMR chemical shifts were referenced to H_3PO_4. The ^{19}F NMR chemical shifts were referenced to $CFCl_3$. ^{11}B NMR chemical shifts were referenced to $[F_3B\cdot OEt_2]$. Mass spectra were recorded using either a VG Autospec or a VG Platform II spectrometer. FTIR spectra were measured using a Perkin-Elmer Spectrum GX spectrometer. Elemental analyses were performed by the Science Technical Support Unit at The London Metropolitan University.

Solvents and Reagents. Diethyl ether and tetrahydrofuran were dried by prolonged reflux, under a nitrogen atmosphere, over sodium metal with a benzophenone ketyl indicator and distilled freshly prior to use. Dichloromethane, acetonitrile, hexane, and methyl iodide were dried over calcium hydride and distilled under nitrogen. Toluene and pentane were dried by passing through a column, packed with commercially available Q-5 reagent (13% CuO on alumina) and activated alumina (pellets, 3 mm), in a stream of nitrogen. Methyl acetate was dried over P_2O_5 and distilled under nitrogen. Acetone was dried over B_2O_3 and distilled under nitrogen. Ethanol and methanol were dried

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over sodium and distilled under nitrogen. $[Rh(CO)_2Cl]_2$[42] and $[Rh(CO)_2(OAc)]_2$[43] were prepared according to published procedures. The preparation of $PhB(C_6H_4PPh_2)_2$ was adapted from a procedure described by Bourissou and co-workers.[28]

$PhB(C_6H_4PPh_2)_2$. $HPPh_2$ (2.92 g 16.0 mmol), 1-iodo-2-bromobenzene (7.71 g, 16.2 mmol), and $[Pd(PPh_3)_4]$ (0.1 g, 0.08 mmol) were weighed into a glass ampule before adding NEt_3 (2.8 mL, 20 mmol) and toluene (3 mL). The ampule was sealed and heated to 80 °C. After 14 h the brown suspension was allowed to cool to room temperature before extracting with 6 × 20 mL portions of toluene. Toluene was removed *in vacuo*, and the resultant yellow solid redissolved into toluene (10 mL) and filtered through a 4 cm silica pad (under a nitrogen atmosphere). Four 20 mL portions of toluene were used to wash the product from the silica pad. The toluene was removed *in vacuo* to yield $Ph_2P(C_6H_4Br)$ as an off-white solid (5.1 g, 92% yield). The ESI mass spectrum and NMR data were identical to those reported by Peters.[34]

Freshly dried Et_2O (15 mL) was added to $Ph_2P(C_6H_4Br)$ (1.01 g, 2.96 mmol) before cooling the resultant suspension to 0 °C. ^nBuLi (1.3 mL, 3.11 mmol, 2.5 M) was added dropwise before allowing the suspension to warm to room temperature. The residue was filtered and washed with 2 × 5 mL portions of Et_2O before drying *in vacuo*. The product $Ph_2P(C_6H_4Li)$ (0.7 g, 88% yield) was used without characterization.

$Ph_2P(C_6H_4Li)$ (0.7 g, 2.6 mmol) was suspended in freshly dried toluene (15 mL) and cooled to −78 °C. $PhBCl_2$ (0.206 g, 1.3 mmol) was added dropwise by cannula to the stirring suspension (washing the flask with 3 × 3 mL portions of toluene). The suspension was stirred at −78 °C for 2 h before allowing it to warm to room temperature and stirring for a further 2 h. The supernatant was isolated by filtration before removing the solvent *in vacuo* to yield the product $PhB(C_6H_4PPh_2)_2$ as an off-white solid (0.410 g, 52% yield). ESI/MS^+ (m/z): 611 ($[M]^+$, 100%), 652 ($[M + CH_3CN]^+$, 70%). ^1H NMR (400 MHz, C_6D_6): 6.7−8.0 ppm (m, ArH). ^{31}P NMR (162 MHz, $CDCl_3$): −6.14 ppm (see Supporting Information).

[Rh(CO)Cl(BPP)]. $PhB(C_6H_4PPh_2)_2$ (75 mg, 0.13 mmol) was dissolved in dichloromethane (5 mL) and added dropwise to $[RhCl(CO)_2]_2$ (24 mg, 0.065 mmol) dissolved in dichloromethane (5 mL). The resultant yellow solution was left to stir for 40 min before concentrating the solution (1 mL) and adding pentane to precipitate a yellow solid. The product (85 mg, 65%) was isolated by filtration and dried *in vacuo*. Anal. Found for $C_{43}H_{33}P_2OBClRh$: C, 66.53; H, 4.24. Calcd: C, 66.48; H, 4.28. ^{31}P NMR (162 MHz, $CDCl_3$): *cis* (65%) δ 54.2 (dd, $^2J_{P-P}$ = 36.4, $^1J_{Rh-P}$ = 146.1), 36.3 (dd, $^2J_{P-P}$ = 36.4, $^1J_{Rh-P}$ = 119.2); *trans*-A (29%) δ 33.8 (d, $^1J_{Rh-P}$ = 110.1); *trans*-B (6%) δ 28.4 (d, $^1J_{Rh-P}$ = 106.3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.6 (br). IR (Nujol) ν(CO) 2060, 2013, 1976 cm^{-1}. LSIMS/MS^+ (m/z): 713 ($[M - (CO) - Cl]^+$, 100%), 748 ($[M - (CO) + H]^+$, 30%).

$[Rh(CO)_2(BPP)]SbF_6$. A chloroform solution (20 mL) of [Rh(CO)Cl(BPP)] (0.096 g, 0.123 mmol) was added to a CO-saturated suspension of $AgSbF_6$ (43 mg, 0.123 mmol) in chloroform (10 mL). The resultant suspension was stirred for 6 h under an atmosphere of CO before filtering. The filtrate was concentrated (1 mL) before precipitating the product from solution as a yellow solid (75 mg, 61%) with pentane. The supernatant was removed by filtration, and the residue dried *in vacuo*. Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a dichloromethane solution of the product. Anal. Found for $C_{44}H_{33}P_2O_2F_6BSbRh$: C, 52.49; H, 3.18. Calcd: C, 52.58; H, 3.31. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.5 (d, $^1J_{Rh-P}$ = 119.3). ^{11}B NMR (128 MHz, $CDCl_3$): δ −0.5 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, J values in Hz): δ 178.7 (dd, J = 81.3, J = 58.7, Rh-CO). IR (Nujol): ν(CO), 2123, 2096 cm^{-1}. ESI/MS^+ (m/z): 769 ($[M]^+$, 40%), 713 ($[M - 2(CO)]^+$, 100%). ESI/MS^- (m/z): 235 ($[M]^-$, 100%).

Crystal data for $[Rh(CO)_2(BPP)](SbF_6)$: $[C_{44}H_{33}BO_2P_2Rh](SbF_6)\cdot CH_2Cl_2$, M = 1090.04, monoclinic, $P2_1/c$ (no. 14), a = 18.4627(3) Å, b = 15.58519(17) Å, c = 15.9429(2) Å, β = 110.0615(17)°, V = 4309.14(11) Å^3, Z = 4, D_c = 1.680 g cm^{-3}, μ(Mo Kα) = 1.272 mm^{-1}, T = 173 K, pale brown blocks, Oxford Diffraction Xcalibur 3 diffractometer; 14 435 independent measured reflections (R_{int} = 0.0575), F^2 refinement, R_1(obs) = 0.0377, wR_2(all) = 0.1055, 9106 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 557 parameters. CCDC 807789.

$[Rh(MeCN)_2(BPP)]SbF_6$. $[Rh(CO)_2(BPP)]SbF_6$ (70 mg, 0.07 mmol) was dissolved in acetonitrile (20 mL) and left to stir overnight. The acetonitrile was removed *in vacuo* to yield the product as a yellow solid (63 mg, 88%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a dichloromethane solution of the product. Anal. Found for $C_{46}H_{39}N_2P_2F_6SbBRh$: C, 53.44; H, 3.75; N, 2.66. Calcd: C, 53.58; H, 3.81; N, 2.72. ^{31}P NMR (162 MHz, CD_3CN): δ 54.3 (d, $^1J_{Rh-P}$ = 155.5). ^{11}B NMR (128 MHz, $CDCl_3$): δ 8.1 (br). ^{19}F NMR (377 MHz, CD_3CN): δ −123 (superposition of sextet due to $^{121}SbF_6^-$ and octet due to $^{123}SbF_6^-$). IR (Nujol): ν(CN), 2004 cm^{-1}. ESI/MS^+ (m/z): 795 ($[M]^+$, 3%), 754 ($[M - (MeCN)]^+$, 16%), 713 ($[M - 2(MeCN)]^+$, 100%), LSIMS/MS^- (m/z): 235 ($[M]^-$, 100%).

Crystal data for $[Rh(MeCN)_2(BPP)](SbF_6)$: $[C_{46}H_{39}BN_2P_2Rh](SbF_6)$, M = 1031.20, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.56293(4) Å, b = 17.51545(7) Å, c = 23.79538(10) Å, V = 4402.49(3) Å^3, Z = 4, D_c = 1.556 g cm^{-3}, μ(Cu Kα) = 9.095 mm^{-1}, T = 173 K, yellow blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 8711 independent measured reflections (R_{int} = 0.0360), F^2 refinement, R_1(obs) = 0.0273, wR_2(all) = 0.0724, 8566 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 580 parameters. The absolute structure of $[Rh(MeCN)_2(BPP)](SbF_6)$ was determined by a combination of *R*-factor tests [R_1^+ = 0.0273, R_1^- = 0.0731] and by use of the Flack parameter [x^+ = +0.024(4), x^- = +0.976(4)]. CCDC 807790.

$[B(C_6F_5)_3\cdot MeOAc]$. MeOAc (1 mL) was added to a stirred suspension of $B(C_6F_5)_3$ (88 mg, 0,17 mmol) in pentane (30 mL). After one hour the suspension was filtered. Upon removal of the pentane the product was isolated as a white solid (49 mg, 49%). Anal. Found for $C_{21}H_6O_2F_{15}B$: C, 42.95; H, 0.99. Calcd: C, 43.04; H, 1.03. ^1H NMR (400 MHz, $CDCl_3$): δ 4.09 (s, 3H); 2.14 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ −134.44 (d, 6F, ^3J = 18.8); −155.35 (t, 6F, ^3J = 18.8); −162.83 (t, 6F, ^3J = 18.8). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 20.6 (CH_3), 58.3 (O-CH_3), 116.1 (br, *C*-B), 137.5 (d, $^1J_{C-F}$ = 250.8, Ar *C*-F), 140.9 (d, $^1J_{C-F}$ = 258.3, Ar *C*-F), 148.0 (d, $^1J_{C-F}$ = 242.8, Ar *C*-F), 184.6 (CO_2Me). ^{11}B NMR (128 MHz, $CDCl_3$): δ 4.1 (br). IR (Nujol): 1649 cm^{-1} ν(C=O), 1469 cm^{-1} ν(B−O).

Oxidative Addition Studies with Methyl Acetate and $[Rh(CO)_2(BPP)]SbF_6$. $[Rh(CO)_2(BPP)]SbF_6$ (5 mg, ∼5 μmol) was dissolved in a 4 M methyl acetate solution in $CDCl_3$ (0.5 mL) before heating to 70 °C for seven days in a sealed NMR tube. The reaction was monitored by ^1H NMR and ^{31}P NMR spectroscopy.

Oxidative Addition Studies with Trifluoromethyl Acetate and $[Rh(CO)_2(BPP)]SbF_6$. $[Rh(CO)_2(BPP)]SbF_6$ (5 mg, ∼5 μmol) was dissolved in a 4 M trifluoromethyl acetate solution in $CDCl_3$ (0.5 mL) before heating to 70 °C for seven days in a sealed NMR tube. The reaction was monitored by ^1H NMR and ^{31}P NMR spectroscopy.

Oxidative Addition Studies with Methyl Iodide and $[Rh(CO)_2(BPP)]SbF_6$. $[Rh(CO)_2(BPP)]SbF_6$ (5 mg, ∼5 μmol) was dissolved in a 4 M methyl iodide solution in $CDCl_3$ (0.5 mL) before heating to 70 °C for seven days in a sealed NMR tube. The reaction was monitored by ^1H NMR and ^{31}P NMR spectroscopy.

Oxidative Addition Studies with $[B(C_6F_5)_3\cdot MeOAc]$ and $[Rh(OAc)(CO)_2]_2$. $[MeOAc\cdot B(C_6F_5)_3]$ (5 mg, 12 μmol) and $[Rh(OAc)(CO)_2]_2$ (3.3 mg, 5.7 μmol) were dissolved in C_6D_6 (0.5 mL) before heating to 70 °C for seven days in a sealed NMR tube. The reaction was monitored by ^1H, ^{11}B, and ^{19}F NMR spectroscopy.

Methyl Acetate Carbonylation Studies without LiI. A rhodium compound (42 μmol) was dissolved in anhydrous MeOAc (38 g, 0.51 mol)

before transferring to a nitrogen-purged, 300 mL, high-pressure reactor. The reactor was then pressurized with CO (40 bar) and heated at 130 °C for 16 h. Upon cooling to 5 °C the CO was vented from the reactor and the reaction mixture weighed. A 150 mg aliquot of the reaction mixture was weighed into a vial with 50 mg of MeCN before mixing and analyzing by ^{1}H NMR in d_6-dmso. The molar composition of the reaction mixture was determined by calculating the areas of the ^{1}H NMR peaks relative to the MeCN standard.

■ ASSOCIATED CONTENT

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

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■ REFERENCES

(1) Haynes, A. *Adv. Catal.* **2010**, *53*, 1.
(2) Haynes, A. *Top. Organomet. Chem.* **2006**, *18*, 179.
(3) van Leeuwen, P. W. N. M. In *Homogeneous Catalysis*; Kluwer Academic Publishers: Dordrecht, 2004; p 109.
(4) Tremblay, J.-F. *Chem. Eng. News* **2009**, 22.
(5) Ellis, B.; Howard, M. J.; Joyner, R. W.; Reddy, K. N.; Padley, M. B.; Smith, W. J. *Stud. Surf. Sci. Catal.* **1996**, *101*, 771.
(6) Bhan, A.; Allian, A. D.; Sunley, G. J.; Law, D. J.; Iglesia, E. *J. Am. Chem. Soc.* **2007**, *129*, 4919.
(7) Blasco, T.; Boronat, M.; Concepción, P.; Corma, A.; Law, D. J.; Vidal-Moya, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 3938.
(8) Boronat, M.; Martinez-Sanchez, C.; Law, D.; Corma, A. *J. Am. Chem. Soc.* **2008**, *130*, 16316.
(9) Wegman, R. W. *J. Chem. Soc., Chem. Commun.* **1994**, 947.
(10) Bagno, A.; Bukala, J.; Olah, G. A. *J. Org. Chem.* **1990**, *55*, 4284.
(11) Smith, W. J. (BP Chemicals Ltd., UK) EP596632, 1994.
(12) Smith, W. J. (BP Chemicals Ltd., UK) WO085162, 2005.
(13) Church, T. L.; Getzler, Y.; Byrne, C. M.; Coates, G. W. *Chem. Commun.* **2007**, 657.
(14) Church, T. L.; Getzler, Y.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 10125.
(15) Kramer, J. W.; Lobkovsky, E. B.; Coates, G. W. *Org. Lett.* **2006**, *8*, 3709.
(16) Kang, F. A.; Sui, Z. H.; Murray, W. V. *J. Am. Chem. Soc.* **2008**, *130*, 11300.
(17) Lu, Y.; Arndtsen, B. A. *Org. Lett.* **2007**, *9*, 4395.
(18) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
(19) Xu, H. Y.; Jia, L. *Org. Lett.* **2003**, *5*, 3955.
(20) Faust, R.; Kennedy, J. P. *J. Polym. Sci. A* **1987**, *25*, 1847.
(21) Beckett, M. A.; Brassington, D. S.; Coles, S. J.; Hursthouse, M. B. *Inorg. Chem. Commun.* **2000**, *3*, 530.
(22) Mitu, S.; Baird, M. C. *Can. J. Chem.* **2006**, *84*, 225.
(23) Britovsek, G. J. P.; Taylor, R. A.; Sunley, G. J.; Law, D. J.; White, A. J. P. *Organometallics* **2006**, *25*, 2074.
(24) Taylor, R. A.; Law, D. J.; Sunley, G. J.; White, A. J. P.; Britovsek, G. J. P. *Chem. Commun.* **2008**, 2800.
(25) Taylor, R. A.; Law, D. J.; Sunley, G. J.; White, A. J. P.; Britovsek, G. J. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 5900.
(26) Conifer, C. M.; Taylor, R. A.; Law, D. J.; Sunley, G. J.; White, A. J. P.; Britovsek, G. J. P. *Dalton Trans.* **2011**, *40*, 1031.
(27) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Mique, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611.
(28) Bontemps, S.; Sircoglou, M.; Bouhadir, G.; Puschmann, H.; Howard, J. A. K.; Dyer, P. W.; Mique, K.; Bourissou, D. *Chem.—Eur. J.* **2008**, *14*, 731.
(29) Sircoglou, M.; Bontemps, S.; Mercy, M.; Mique, K.; Ladeira, S.; Saffon, N.; Maron, L.; Bouhadir, G.; Bourissou, D. *Inorg. Chem.* **2010**, *49*, 3983.
(30) Braunschweig, H.; Dewhurst, R. D. *Dalton Trans.* **2011**, *40*, 549.
(31) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056.
(32) Pang, K. L.; Tanski, J. M.; Parkin, G. *Chem. Commun.* **2008**, 1008.
(33) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583.
(34) Whited, M. T.; Rivard, E.; Peters, J. C. *Chem. Commun.* **2006**, 1613.
(35) Harder, S.; Brandsma, L.; Kanters, J. A.; Duisenberg, A.; van Lenthe, J. H. *J. Organomet. Chem.* **1991**, *420*, 143.
(36) Hudnall, T. W.; Kim, Y. M.; Bebbington, M. W. P.; Bourissou, D.; Gabbai, F. P. *J. Am. Chem. Soc.* **2008**, *130*, 4222.
(37) Bätzel, V.; Müller, U.; Allmann, R. *J. Organomet. Chem.* **1975**, *102*, 109.
(38) Chipperfield, A. K.; Housecroft, C. E.; Raithby, P. R. *Organometallics* **1990**, *9*, 479.
(39) Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta* **1973**, *7*, 393.
(40) Shriver, D. F.; Alich, S. A. *Coord. Chem. Rev.* **1972**, *8*, 15.
(41) Bellachioma, G.; Cardaci, G.; Foresti, E.; Macchioni, A.; Sabatino, P.; Zuccaccia, C. *Inorg. Chim. Acta* **2003**, *353*, 245.
(42) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.
(43) Wilson, J. M.; Sunley, G. J.; Adams, H.; Haynes, A. *J. Organomet. Chem.* **2005**, *690*, 6089.