Lewis-Acidity of Trimethylplatinum(IV) with Labile Oxygen-Donor Ligands

Vicki Hsieh,[†] Antonio G. De Crisci,[†] Alan J. Lough,[‡] and Ulrich Fekl*,[†]

Department of Chemical and Physical Sciences, UTM, University of Toronto, 3359 Mississauga Road N, Mississauga, Ontario, Canada L5L 1C6, and X-ray Crystallography Lab, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

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Trimethylplatinum(IV) systems with labile ligands and weakly coordinating anions were investigated with respect to their Lewis-acidity and their ability to act as Lewis-acidic catalysts. The Lewis-acidity of tetrameric trimethylplatinum(IV) triflate (triflate = trifluoromethanesulfonate, OTf), [{Me_3PtOTf}$_4$], toward carbonyl compounds was quantified by NMR titration with crotonaldehyde (Childs' method) in CD_2Cl_2. The data show moderate but significant Lewis-acidity of the trimethyl platinum(IV) center (27% of the acidity of BBr_3) and commensurate (moderate) intrinsic catalytic activity of the trimethylplatinum(IV) unit. Crystals of an aldehyde adduct were obtained. X-ray crystallography shows a binuclear metal complex, [{Me_3Pt(crotonaldehyde)(μ-OTf)}$_2$]. Despite the relatively low Lewis-acidity, in the absence of oxygen-donor ligands, the trimethylplatinum(IV) is capable of decomposing the $[B(Ar^F)_4]^-$ anion (Ar^F = 3,5-$(CF_3)_2C_6H_3$) to yield $B(Ar^F)_3$, apparently via aryl abstraction. Salt metathesis reactions of [{Me_3PtOTf}$_4$] with $Na[B(Ar^F)_4]$ in the presence of oxygen-donor ligands lead to mixtures that are highly catalytically active in the diastereoselective Mukaiyama-aldol reaction, likely via generation of very electrophilic silicon species.

Introduction

Lewis acids are powerful tools in the hands of the synthetic organic chemist since they can enhance rates for many reactions and can increase yield and selectivity. Lewis acids based on transition metals often offer advantages: many systems, in particular those based on second- and third-row transition metals, are less oxophilic than "classic" Lewis acids (aluminum or boron halides), and inhibition by product or adventitious water can often be prevented with transition metal Lewis acids.[1] Well-designed transition metal systems can offer the high ligand exchange rates needed for turnover, and a catalytic amount of the Lewis acid might be sufficient, rather than a stoichiometric amount (normally needed for traditional systems). Tuning of stereoselectivity is generally very feasible since the design of spectator ligands for transition metals is highly developed. Also, complexes can often be designed such that more than one Lewis-acidic site is present and generally within a well-defined geometry. Examples are square-planar "L_2"$M(solv)_2^{2+}$ cations (M = Pt, Pd), where two *cis* positions are blocked by the spectator ligand "L_2" such that two labile solvent molecules (solv) create two Lewis-acidic sites in *cis* arrangement. Such systems are of growing importance, and mechanisms often invoke utilization of both Lewis-acidic sites.[2] Catalysts having *three* Lewis-acidic sites in a well-defined geometry have proven useful already. However, examples exist mainly for meridionally three-point binding acids, and facially three-point binding acids are rare.[1,3] Systems having *fac* geometry appear promising for cooperative action of all three acidic sites. Thus, we may consider pseudo-octahedral complexes ideally having a d^6 electron count (a well-defined geometry around the metal center is likely important for controlling stereoselectivity of metal-catalyzed reactions), where three facial positions are occupied by strongly bonded ligands and the remaining three positions are labile: a *fac*-$L_3M(solv)_3^{z+}$ cation as the active species. Extremely strong Lewis acids are useful for stoichiometric reactions, but generally exhibit too low substitution rates to be of synthetic use. A good catalyst is moderately Lewis-acidic. In order to achieve catalytic turnover, substitution reactions at the metal should be fast. Even in low-spin d^6 systems, traditionally considered "inert", fast ligand substitution can be achieved if a strong σ-donor, for example an alkyl, is present in *trans* position. A particularly stable metal trialkyl unit can be found in the solvated trimethylplatinum(IV) complexes, $Me_3Pt(solv)_3^+$, which has been shown to act as three-point binding in interaction with carbohydrates.[4] Ligand exchange is expected to be sufficiently fast since water exchange at $Me_3Pt(OH_2)_3^+$ occurs on the millisecond time scale.[5] In addition, stereochemistry at the metal will be well-defined: all trimethylplatinum(IV) complexes structurally characterized so far are six-

* Corresponding author. E-mail: ufekl@utm.utoronto.ca.
[†] Department of Chemical and Physical Sciences.
[‡] X-ray Crystallography Lab.

(1) Yamamoto, H., Ed. *Lewis Acids in Organic Synthesis. A Comprehensive Handbook in Two Volumes*; Wiley-VCH: Weinheim, 2000.

(2) (a) Dutcă, L.-M.; Ko, K.-S.; Pohl, N. L.; Kostić, N. M. *Inorg. Chem.* **2005**, *44*, 5141. (b) Milović, N. M.; Dutcă, L.-M.; Kostić, N. M. *Chem.−Eur. J.* **2003**, *9*, 5097. (c) Milović, N. M.; Kostić, N. M. *J. Am. Chem. Soc.* **2003**, *125*, 781. (d) Brunkan, N. M.; White, P. S.; Gagné, M. R. *Organometallics* **2002**, *21*, 1565. (e) Brunkan, N. M.; Gagné, M. R. *Organometallics* **2002**, *21*, 1576. (f) Michelin, R. A.; Pizzo, E.; Scarso, A.; Sgarbossa, P.; Strukul, G.; Tassan, A. *Organometallics* **2005**, *24*, 1012. (g) Brunetta, A.; Strukul, G. *Eur. J. Inorg. Chem.* **2004**, 1030. (h) Cendron, A.; Strukul, G. *J. Mol. Catal. A* **2003**, *204*−205, 187. (i) Gavagnin, R.; Cataldo, M.; Pinna, F.; Strukul, G. *Organometallics* **1998**, *17*, 661. (j) Hattori, T.; Suzuki, Y.; Uesugi, O.; Oi, S.; Miyano, S. *J. Chem. Soc., Chem. Commun.* **2000**, 73.

(3) (a) Evans, D. A.; Downey, C. W.; Hubbs, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 8706. (b) Itoh, K.; Kanemasa, S. *J. Am. Chem. Soc.* **2002**, *124*, 13394.

(4) (a) Junicke, H.; Steinborn, D. *Inorg. Chim. Acta* **2003**, *346*, 129. (b) Junicke, H.; Bruhn, C.; Kluge, R.; Serianni, A. S; Steinborn, D. *J. Am. Chem. Soc.* **1999**, *121*, 6232. (c) Junicke, H.; Bruhn, C.; Ströhl, D.; Kluge, R.; Steinborn, D. *Inorg. Chem.* **1998**, *37*, 4603.

(5) Glass, G. E.; Tobias, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 6371.

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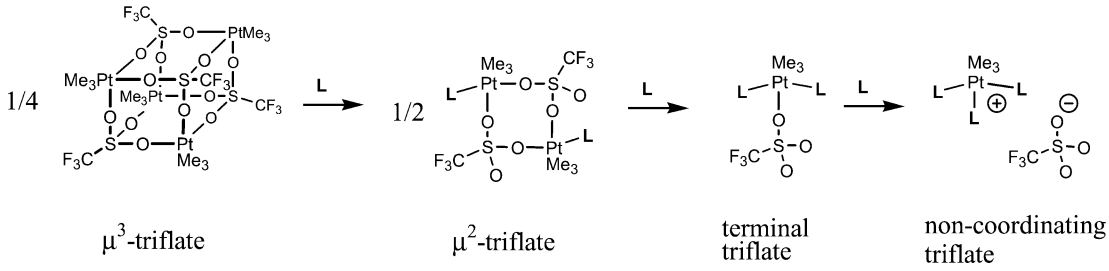
Scheme 1



coordinate and pseudo-octahedral, with the only exception of [(nacnac)$PtMe_3$] (nacnac = {(2,6-^{i}Pr$_2$-C_6H_3)NC(Me)}$_2$CH), which is five-coordinate, exhibiting square-pyramidal structure in the solid state.[6] By virtue of being square-pyramidal, even this exception is essentially based on an octahedron, since a square pyramid resembles an octahedron having one open site. Despite these promising properties, the potential of the trimethylplatinum(IV) unit for *catalytic* use as a three-point binding Lewis acid has not been investigated. Even the Lewis acid strength of the trimethylplatinum(IV) unit is not known. Here, we report our results on the Lewis-acidity of the trimethylplatinum(IV) unit in pseudo-octahedral complexes having labile anionic and neutral oxygen-donor ligands.

Results and Discussion

Trimethylplatinum(IV) Triflate. Trimethylplatinum triflate (triflate = trifluoromethanesulfonate, $F_3CSO_3^-$, OTf $^-$) exists as a tetrameric heterocubane species where each platinum center is octahedrally coordinated and each triflate coordinates to three platinum centers. Triflate is relatively labile, and added ligands L can force it to switch into lower coordination modes ($\mu^3 \rightarrow \mu^2 \rightarrow$ terminal) and eventually into a noncoordinating mode, as shown in Scheme 1.[7] We quantified the Lewis-acidity of trimethylplatinum triflate by means of NMR titration with crotonaldehyde, and we began to test for catalytic activity in selected reactions that are typically enhanced by Lewis-acidic catalysts.

Lewis-Acidity. To determine the Lewis-acidity of trimethylplatinum triflate, we used the NMR method developed by Childs, Mulholland, and Nixon.[8] This empirical method has received theoretical support,[9] and it involves formation of a Lewis acid/Lewis base adduct where the carbonyl oxygen of an α,β-unsaturated compound coordinates to the Lewis acid. Particularly the change in ^{1}H chemical shift for the olefinic hydrogen in β-position (at the C3-carbon), compared to uncomplexed base, is an excellent indicator of relative acidity of the Lewis acid. Crotonaldehyde is most commonly used as the Lewis base. A positive shift difference $\Delta\delta$ (downfield shift) is expected as a consequence of the electron-withdrawing (deshielding) effect of a Lewis acid. A known amount of crotonaldehyde (*trans*-2-butenal, 0.1 mmol in 0.57 mL of CD_2Cl_2) was titrated with trimethylplatinum triflate, by stepwise adding small amounts of trimethylplatinum triflate, each step involving ca. 10 mol % Pt, relative to crotonaldehyde. As expected, all proton resonances of crotonaldehyde were found to be shifted—some slightly, some considerably—upon complexation with the trimethylplatinum species, added as [{Me_3PtOTf}$_4$]. The ^{1}H NMR signals of complexed and free crotonaldehyde were not observed as separate signals but were in rapid exchange such that the observed shift, at room temperature, was the weighted average for complexed and free crotonaldehyde. Figure 1 shows a plot of the observed change in chemical shift, $\Delta\delta$, for the β-hydrogen versus equivalents of Pt added. The observed value for $\Delta\delta$ converges rapidly to yield $\Delta\delta = 0.40$ ($\pm$0.01) ppm, and just after the addition of ca. 1 equiv of Pt, the observed shift change is indistinguishable, within the error of the measurement, from the final limiting value. This limiting value would correspond to a situation where for each molecule of aldehyde such an excess of platinum is available that each crotonaldehyde molecule is bonded to platinum. Provided that crotonaldehyde acts only as a terminal (nonbridging) ligand, it would follow that any given molecule of crotonaldehyde is bonded to exactly one Me_3Pt(IV) unit.

The dimeric type of structure shown as "μ^2-triflate" in Scheme 1 would allow for this 1:1 stoichiometry. An X-ray structure of an aldehyde adduct crystallizing from such a reaction mixture will be discussed below, and a dimeric structure involving bridging triflate is indeed observed. Under conditions where the aldehyde concentration is higher than the platinum concentration, structures containing two molecules of aldehyde per Pt ("terminal triflate" in Scheme 1) or even three ("noncoordinating triflate") aldehydes will also exist.[10] In our pursuit of a Me_3-Pt(crotonaldehyde)$_3^+$ cation, we performed $AgBF_4$ metathesis on (tetrameric) trimethylplatinum iodide in the presence of 3 equiv of crotonaldehyde in CD_2Cl_2 solvent. Such a sample, apparently containing Me_3Pt(crotonaldehyde)$_3^+BF_4^-$ as the major species, shows somewhat broadened signals for coordinated aldehyde and gives a shift change for the β-hydrogen $\Delta\delta = 0.34$ ppm. The true value of $\Delta\delta$ for Me_3Pt(crotonaldehyde)$_3^+$ might be higher because the observed value may be an averaged value containing some contribution from free crotonaldehyde. Therefore, the limiting value $\Delta\delta = 0.40$ ppm, obtained in the presence of excess Pt (>1.2 equiv), is arguably a more accurate determination of the electron-withdrawing effect of the Me_3Pt-(IV) unit on the β-hydrogen of crotonaldehyde. The observed $\Delta\delta(^1H)$ for the β-hydrogen (0.40 ppm) correlates extremely well with the $\Delta\delta(^{13}C)$ of carbon C3. Using Childs' empirical relation[8] for C3/H3, namely, $\Delta\delta(^{13}C) = 22.3\Delta\delta(^1H) - 0.1$ ppm, a shift change $\Delta\delta(^{13}C)$ of 8.8 ppm would be predicted for C3. A ^{13}C experiment yields $\Delta\delta(^{13}C) = 9.1$ ppm. Childs' method allows conveniently comparing Lewis acids, and the convention is to relate their β-hydrogen-based crotonaldehyde $\Delta\delta$ to the corresponding value obtained for the very strong Lewis acid BBr_3 ($\Delta\delta = 1.49$), which is arbitrarily assigned a relative Lewis acidity of 1.[8] "Me_3PtOTf" in CD_2Cl_2 thus has a relative Lewis-

(6) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.

(7) Schlecht, S.; Magull, J.; Fenske, D.; Dehnicke, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 1994.

(8) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(9) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.

(10) This is apparent from Figure 1: at 0.5 equiv of Pt, $\Delta\delta$ is already at 85% of the limiting value, showing that more than one aldehyde binds under such conditions. If just free aldehyde and 1:1 complex were in equilibrium, $\Delta\delta$ would be at 50% of the limiting value.

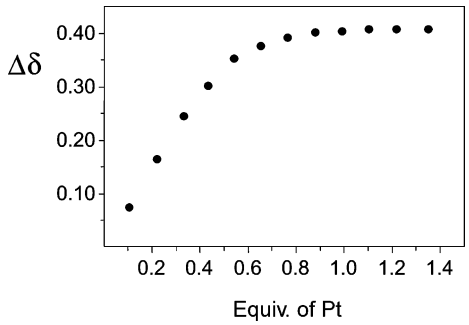


Figure 1. ^{1}H chemical shift difference ($\Delta\delta$ in ppm) of the β-hydrogen (H3) of crotonaldehyde (180 mM in CD_2Cl_2), at 20 °C, upon adding increasing amounts of trimethylplatinum(IV) (equivalents of $PtMe_3$ units are shown), added in the form of [{Me_3-PtOTf}$_4$].

acidity of 0.27. This value places it at the lower end of the scale of typical Lewis acids, and we would like to compare it with two Lewis acids of similar strength: the Lewis-acidity of the trimethylplatinum(IV) unit is somewhat lower than that of $CpFe(CO)_2^+$ (0.36), which appears to have some intrinsic catalytic activity, in addition to catalysis by impurities present in the iron system.[11] Trimethylplatinum(IV) seems to be more acidic than the catalytically useful $[(Cy_2PCH_2CH_2PPh_2)W(CO)(NO)]^+$ fragment (apparent relative Lewis-acidity 0.19). However, it was argued that Childs' method underestimates the true acidity of the latter tungsten complex, due to ring-current effects (NMR) of the phenyls on the phosphine, such that the tungsten complex is likely more Lewis-acidic than the apparent value (0.19) suggests.[11] Thus, the relative Lewis-acidity of the trimethylplatinum(IV) unit (0.27) seems to be just below the acidity of the weakly acidic soft metal carbonyls discussed here, just below the synthetically useful threshold of ca. 0.36.

Structure of [{$Me_3Pt(\eta^1$-O═CHCH═CHMe)(μ-OTf)}$_2$]. A crystalline sample of a crotonaldehyde adduct of trimethylplatinum triflate was obtained. An NMR sample from a titration experiment such as described above (containing 1.4 molar equiv of Me_3PtOTf) was kept at −35 °C, until the adduct between trimethylplatinum triflate and crotonaldehyde crystallized. The crystals, colorless blocks, were subjected to a single-crystal X-ray structure determination.[12] The molecular structure was found to be a dimer of the type [{$Me_3Pt(\eta^1$-O═CHCH═CHMe)-(μ-OTf)}$_2$], shown in Figure 2 (relevant bond lengths and angles in the legend). The two Me_3Pt(crotonaldehyde) units are linked by two bridging triflates and are related by crystallographic symmetry (inversion center). The topology observed here, shown as "μ^2-triflate" in Scheme 1, resembles that observed for the THF complex [{Me_3Pt(THF)(μ-OTf)}$_2$].[7] The Pt−O(crotonaldehyde) bond (2.195 Å, Pt−O1 in Figure 2) is significantly shorter, by 0.08 Å, than the average of the Pt−O bonds to the triflate ions (average = 2.272 Å). This likely indicates that aldehyde is a stronger donor to the trimethylplatinum(IV) unit than triflate.

The Pt−O bonds involving Pt-coordinated triflate are of expected lengths, very similar to those obtained for [{Me_3Pt-(THF)(μ-OTf)}$_2$].[7] The bridging S−O bonds, with individual lengths of 1.435 and 1.456 Å, yield an average of 1.446 Å, not significantly different from the length of the terminal S−O bond (1.444 Å), and the S−O bond seems to be weakly affected by the coordination to Pt. Platinum is six-coordinate in this complex

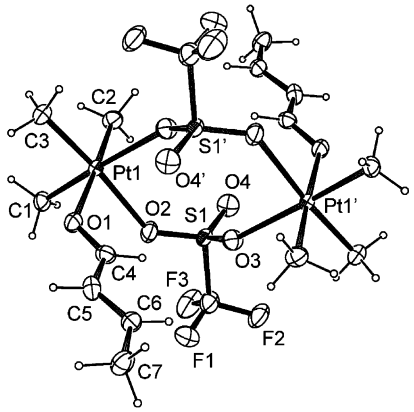


Figure 2. Thermal ellipsoid plot (30% probability, except for hydrogens, which are shown as spheres of arbitrary radius) for [{$Me_3Pt(\eta^1$-crotonaldehyde)(μ-OTf)}$_2$]. The center of the eight-membered ring is a crystallographic inversion center. Selected distances and angles (Å, deg): Pt1−C1, 2.011(7); Pt1−C2, 2.007-(8); Pt1−C3, 1.998(7); Pt1−O1, 2.195(5); Pt1−O2, 2.266(5); Pt1−O3′, 2.278(6); S1−O2, 1.435(6); S1−O3, 1.456(6); S1−O4, 1.444(6); O1−C4, 1.240(9); C4−C5, 1.421(11); C5−C6, 1.318-(11); C6−C7, 1.493(11); C1−Pt1−C2, 88.8(3); C1−Pt1−C3, 91.3-(3); C2−Pt1−C3, 89.0(3); C1−Pt1−O1, 90.9(3); C2−Pt1−O1, 177.6(3); C1−Pt1−O3′, 173.3(3); O1−Pt1−O3′, 94.1(2); O2−Pt1−O3′, 90.9(2); O1−Pt1−O2, 88.3(2); Pt1−O1−C4, 125.8(5); torsion Pt1−O1−C4−C5, 171.7(3).

and only marginally deviates from octahedral geometry. The aldehyde adopts an *E*-configuration around the carbonyl bond. The Pt1−O1-C4−C5 torsion angle is 171.7°. The Pt1−O1−C4 bond angle is 125.8°. This angle is close to the 120° angle expected for sp^2-hybridization at oxygen. Very similar geometric features involving η^1-bonded crotonaldehyde were reported for crotonaldehyde bonded to the tungsten fragment [TpW(CO)-(PhCCMe)] (Tp = tris(pyrazolyl)borate), but the bond angle around the carbonyl oxygen was larger (139.0°) in the tungsten example, very likely due to the steric demand of the Tp ligand.[13] For the C═O bond length and the C═C bond length, very similar values were found in the present platinum complex and in the tungsten complex discussed above, namely, 1.240(9) vs 1.232(8) Å (C═O) and 1.421(11) vs 1.423(10) Å (C═C), respectively. The question arises as to whether the conformation and the binding mode of the aldehyde observed in the solid-state structure resemble the binding mode in solution. The NMR data (see Experimental Section) indicate that this is indeed the case. First, there is strong spectroscopic evidence that coordinated crotonaldehyde is the *s-trans* isomer in solution. The *s-trans* isomer is the crystallographically observed isomer and, for free crotonaldehyde, also the thermodynamically preferred isomer. In solution, the vicinal $^3J_{HH}$ coupling between the α-proton (O═CHC*H*═) and the aldehydic proton (CHO) is indicative of either *cis* or *trans* geometry,[14] and the value we obtain for the coordinated crotonaldehyde (8 Hz) corresponds to the *s-trans* conformation. With regard to the question whether aldehyde acts as a σ-donor (η^1, as observed in the solid state) or possibly as a π-donor (η^2), we observe that the ^{1}H NMR shift of the aldehydic proton (CHO) remains virtually unchanged from that of free crotonaldehyde ($|\Delta\delta| < 0.01$ ppm). Small shift differences for the aldehydic proton (typically 0−2 ppm) are characteristic for terminally (η^1) metal-bonded aldehydes, and large shift differences (δ shifted upfield by more than 2.5 ppm) would be expected for η^2-aldehyde.[13] Furthermore, we observe

(11) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *11*, 6070.

(12) Details are given in the Experimental Section.

(13) Schuster, D. M.; White, P. S.; Templeton, J. L. *Organometallics* **2000**, *19*, 1540.

(14) McNab, H. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1283.

a ^{13}C chemical shift of 202 ppm for the carbonyl oxygen. Such a shift, largely unperturbed from free crotonaldehyde (194 ppm), is indicative of the η^1-binding mode, whereas the carbonyl resonances for η^2-complexes are strongly upfield shifted, by typically 100 ppm.[13] Thus, the NMR data show that crotonaldehyde is η^1-bonded in solution, too.

Catalytic Activity of Trimethylplatinum(IV) Triflate. We investigated the catalysis of Diels−Alder reactions where the dienophile contains a potentially coordinating oxygen functionality. We found that the room-temperature Diels−Alder reaction between 1,2,3,4,5-pentamethylcyclopentadiene (Cp*H) and dimethylmaleate is significantly sped up if [{Me_3PtOTf}$_4$] is added. When 5 mol % of Pt was used to catalyze the reaction between the above reactants, both initially present at 180 mM concentration in CD_2Cl_2 solvent, the reaction was complete within 5.5 h, as observed by ^1H NMR spectroscopy. When the reaction was finished, an NMR analysis employing an internal standard showed that the Diels−Alder adduct was obtained in 83.5% yield. The only detectable side-products were assigned as polymerized/oligomerized Cp*H, and due to this loss of Cp*H, a small amount of unreacted dimethylmaleate was also present when the reaction stopped.[15] The Diels−Alder adduct formed was exclusively the *anti-endo* adduct.[16,17] The uncatalyzed reaction took 10 days to complete. While [{Me_3PtOTf}$_4$] indeed functioned as a catalyst precursor, this does not necessarily mean the Me_3Pt(IV) unit has to be directly involved in the catalysis observed. For example, it is known that a metal complex sometimes simply acts to produce H^+.[11,18] Since triflic acid (HOTf) itself is an efficient catalyst for the Diels−Alder reaction, we ran a control experiment with 15% HOTf. The reaction appeared to be complete after 5 min when catalyzed by 15% HOTf. It is thus very likely that species other than trimethylplatinum(IV) species are responsible for catalysis in this particular reaction. The formation of new Lewis acids and Brønsted acids was indicated by ^1H NMR spectroscopy on a stoichiometric reaction between Cp*H and [{Me_3PtOTf}$_4$], employing equimolar amounts of Cp*H and Pt. We found that in this control reaction more than 50% of the [{Me_3PtOTf}$_4$] was converted into [Cp*$PtMe_2OTf$].[19] The latter complex has been previously synthesized by protonating Cp*$PtMe_3$ with triflic acid, showing a very characteristic ^1H NMR spectrum of [Cp*$PtMe_2OTf$].[20] For its formation in the reaction of tetrameric trimethylplatinum triflate with Cp*H, we propose the following reaction sequence: 1/4 [{Me_3PtOTf}$_4$] + Cp*H → Cp*$PtMe_3$ + HOTf → [Cp*$PtMe_2OTf$] + CH_4. Both the triflate complex [Cp*$PtMe_2OTf$] and residual acid, generated in the first step, might contribute to the catalysis observed for the reaction between Cp*H and a dienophile. Thus, Diels−Alder reactions involving cyclic dienes would harbor at least an ambiguity as to whether or not a Me_3Pt(IV) species is the true catalyst. Thus, studies aimed at exploring the potential of trimethylplatinum(IV) fragments as actual catalysts have to be carried out with acyclic dienes. We performed such experiments, and the reaction between methacrolein (2-methyl-2-propenal) and isoprene (2-methyl-1,3-butadiene), to form the expected 1,4-adduct,[21] was catalyzed by 5% of [{Me_3PtOTf}$_4$]. Using stoichiometric amounts of the reactants at ca. 350 mM concentration, 50% conversion to product was observed within 18 days. During this time, the uncatalyzed reaction produced only traces of product. However, surprisingly, the catalyzed reaction slowed down and essentially came to a halt after ca. 20 days and roughly 10 turnovers.

Attack of Trimethylplatinum(IV) on the B−C Bond of $B(Ar^F)_4^-$. Having obtained a quantitative measure of the Lewis-acidity of trimethylplatinum(IV) triflate and having shown that trimethylplatinum(IV) triflate can coordinate to aldehydes, we focused on the counterion. The counterion is not entirely innocent under all reaction conditions since triflate was clearly able to coordinate. This makes it worthwhile investigating less coordinating anions,[22] such as $[B(Ar^F)_4]^-$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$), and we tried to obtain monomeric $Me_3Pt[B(Ar^F)_4]$.[23] We attempted a salt metathesis reaction, using $Na[B(Ar^F)_4]$ on [{Me_3PtOTf}$_4$], with the aim of exchanging triflate for the bulky tetraarylborate anion. This appears particularly promising if nonpolar solvents are used, since the small triflate ion should contribute to the driving force of such a reaction via the lattice energy of sodium triflate. Salt metathesis reactions on [{Me_3PtOTf}$_4$], where KOTf precipitated, have recently been used to synthesize the first stable coordinatively unsaturated platinum(IV) alkyl complexes.[6,24] We found that the use of benzene allows for dissolving both [{Me_3PtOTf}$_4$] and $Na[B(Ar^F)_4]$ to sufficient extent, and a reaction does indeed occur at room temperatue in the absence of oxygen-donating ligands: the colorless solution, over a period of a few hours, however, produces a black, insoluble precipitate (see Experimental Section). Following this reaction by ^1H NMR spectrocopy in C_6D_6 shows that some [{Me_3PtOTf}$_4$] (δ 1.26 ppm, J_{Pt-H} = 81.6 Hz) can still be observed after mixing, but rapidly vanishes. After 45 min, [{Me_3PtOTf}$_4$] has virtually completely disappeared, and a complex product mixture is indicated by a large number of new peaks. An analysis of the complex mixture was not attempted, but it is a significant observation that, after removal of the precipitate, clear, white crystals can be grown, by removing the solvent under vacuum. The unit cell parameters of the crystalline species were obtained by single-crystal X-ray diffraction and demonstrated that these crystals are $B(Ar^F)_3$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$), previously crystallographically characterized by Konze, Scott, and Kubas.[25] This 1999 paper reported the first example of B−C bond cleavage in the $[B(Ar^F)_4]^-$ anion mediated by a transition metal species, and *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)]^+$ was used.[25] The dissolved $[(Ph_3P)_2Pt(Me)(OEt_2)]^+$-$[B(Ar^F)_4]^-$ salt was stable only at temperatures below −30 °C, and at room temperature the complex decomposed within days, to produce $B(Ar^F)_3$. In our case of attempted synthesis of $[Me_3Pt][B(Ar^F)_4]$, degradation of $[B(Ar^F)_4]^-$ appears complete within a matter of hours at room temperature. This suggests that the

(15) The fact that the side products stem from Cp*H alone was confirmed by reacting Cp*H with catalytic amounts of $[Me_3PtOTf]_4$, in the absence of a dienophile.

(16) Stereochemistry confirmed by NOE spectroscopy (Experimental Section).

(17) For the uncatalyzed reaction of Cp*H with other (somewhat related) dienophiles: Letourneau, J. E.; Wellman, M. A.; Burnell, D. J. *J. Org. Chem.* **1997**, *62*, 7272.

(18) Wabnitz, T. C.; Yu, J.-Q.; Spencer, J. B. *Chem.−Eur. J.* **2004**, *10*, 484.

(19) As demonstrated by ^1H NMR spectroscopy in CD_2Cl_2 solvent. Interestingly, this reaction produced a deep bluish-purple color. However, this color is not caused by a platinum species, since a control experiment, reacting Cp*H with HOTf, produced the same color, and it is concluded that a trace amount of a deeply colored organic species is responsible for the deep color. Both [Cp*$PtMe_2OTf$] and $[Me_3PtOTf]_4$ are virtually colorless.

(20) Howard, W. A.; Bergman, R. G. *Polyhedron* **1998**, *17*, 803.

(21) For spectroscopic data on the 1,4-adduct, see: Teo, Y.-C.; Loh, T.-P. *Org. Lett.* **2005**, *7*, 2539.

(22) For a review on weakly coordinating anions: Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(23) Metal complexes containing coordinated $B(Ar^F)_4^-$ are known: Powell, J.; Lough; A; Saeed, T. *J. Chem. Soc., Dalton Trans.* **1997**, 4137.

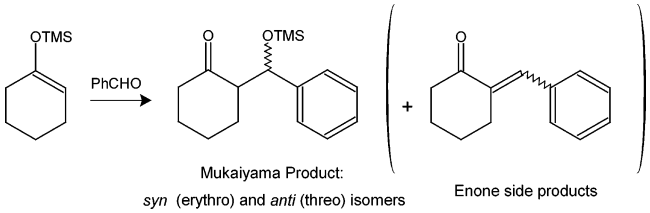
(24) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286.

(25) Konze, W. V.; Scott, B. L.; Kubas, G. J. *Chem. Commun.* **1999**, 1807.

trimethylplatinum(IV) unit may be even more reactive toward cleaving the B−C bond. Its small size may contribute to making attack at the B−C bond of a bulky triarylborate facile. Thus, although [{Me_3PtOTf}$_4$] is not extremely electrophilic, attempts to create free Me_3Pt^+ lead to decomposition reactions that indicate the involvement of an extremely electrophilic species. It is consistent with this view that we observed neither decomposition of the solution nor precipitation of sodium triflate when we performed a similar reaction in THF. In fact, THF complexes of trimethylplatinum(IV) are known to be stable,[26] and coordination of THF apparently attenuates the electrophilicity. Similarly, the reaction mixture did not decompose to any noticeable extent if at least 3 equiv of crotonaldehyde (per Pt) were present. In the presence of crotonaldehyde and using the $[B(Ar^F)_4]^-$ counterion, a new Me_3Pt unit was observed by ^{1}H NMR spectroscopy (at δ 1.22 ppm), and its $^2J_{Pt-H}$ coupling constant (77 Hz) was significantly smaller than that of the crotonaldehyde−Me_3PtOTf complex (J_{Pt-H} = 80 Hz). We may assign this species as [Me_3Pt(crotonaldehyde)$_3$][$B(Ar^F)_4$]. In a similar experiment, where we used CD_2Cl_2 as the solvent in order to obtain a meaningful number (same solvent) for the shift difference $\Delta\delta$ at the hydrogen on C3 of crotonaldehyde, we obtained a $\Delta\delta$ of 0.41 ppm, very similar to the value obtained for Pt-coordinated crotonaldehyde in [{$Me_3Pt(\eta^1$-O=CHCH=CHMe)(μ-OTf)}$_2$] described above ($\Delta\delta$ = 0.40 ppm). The ^{1}H NMR peaks for $[B(Ar^F)_4]^-$ were present, and there was no evidence for decomposition of this anion under these conditions.

Mukaiyama-Aldol Reaction, Catalyzed by Systems Generated from [{Me$_3$PtOTf}$_4$] and Na[B(Ar^F)$_4$]. While we have not obtained $Me_3Pt[B(Ar^F)_4]$ free of additional ligands, addition of oxygen-containing donor ligands L prevents significant decomposition, by allowing for the formation of $[Me_3PtL_3]^+[B(Ar^F)_4]^-$. The oxygen ligand can be one of the reactants of the reaction to be catalyzed. Motivated by this reasoning, we investigated reactions where salt metathesis with $Na[B(Ar^F)_4]$ was performed on [{Me_3PtOTf}$_4$] in the presence of the organic reactants of the reaction to be catalyzed. We found particularly noteworthy results for the Mukaiyama-aldol reaction, the Lewis acid-catalyzed reaction between a silyl enol ether and either an aldehyde or a ketone. However, it will be shown below that the trimethylplatinum(IV) system acts as a precatalyst, generating highly reactive active catalysts that appear to be something other than $[Me_3PtL_3]^+$ compounds. The Mukaiyama reaction was an attractive choice for testing trimethylplatinum(IV) catalysis since the selectivity of this reaction, including stereoselectivity, can strongly depend on which Lewis acid is used.[27] Traditionally, stoichiometric amounts of Lewis acids such as $TiCl_4$ were used.[28] Use of a Lewis acid in *catalytic* amounts is desirable, and more recently several Lewis-acidic catalysts for the Mukaiyama-aldol reaction were reported, Me_3SiOTf, Sc(OTf)$_3$, Me_2AlCl, $^iPr_3Si^+$ $[B(OTf)_4]^-$, and $Cp_2Zr(OTf)_2$, among others.[29] A possible complication with the Mukaiyama-aldol reaction is the formation of undesired side-products such as enones.[30] For this reason, this reaction is often performed at temperatures below 0 °C.[29,30] We investigated catalysis of the Mukaiyama-aldol reaction between 1-cyclohexenyl-OTMS and benzaldehyde. Possible products are shown in Scheme 2.

Scheme 2



We found that *in situ* $Na[B(Ar^F)_4]$ metathesis on [{Me_3PtOTf}$_4$] (5 mol % Pt) creates a catalytic system that is able to achieve stereoselectivity for the *anti* (*threo*) isomer of the desired trialkylsilyl aldolate in high yields at room temperature. The procedure involves adding reactants (silyl enol ether and aldehyde) and 5% $Na[B(Ar^F)_4]$ in dry, chlorinated solvent (CD_2Cl_2 or $CDCl_3$) and, as the last step, generating the catalyst in situ under vigorous shaking, [{Me_3PtOTf}$_4$] (Pt equimolar to $Na[B(Ar^F)_4]$). The ^{1}H NMR spectrum of the reaction mixture after 5 min is remarkably clean, showing the complete disappearance of a telltale peak at 4.86 ppm corresponding to the olefinic proton in 1-cyclohexenyl-OTMS, which shows that the starting material has been consumed in the reaction. Two doublets appear at 5.02 and 5.27 ppm (in $CDCl_3$), corresponding to the HC−OSi protons of the *anti* and *syn* aldolates respectively.[27] Mass balance was quantitative, as shown by ^{1}H NMR spectroscopy employing an internal standard, and no side-products (such as enones) were formed. Reproducibly, good *anti:syn* (=*threo*:*erythro*, determined by ^{1}H NMR spectroscopy) ratios were observed, 72:28 when the reaction was performed in $CDCl_3$ and 75:25 in CD_2Cl_2. The question arises to whether aldehyde-ligated trimethylplatinum(IV)$^+$ is truly the catalytically active species, or rather a catalytically active decomposition product generated in small amounts. We prepared a sample of Me_3Pt(benzaldehyde)$_3^+BF_4^-$ and found it ineffective as a catalyst. Thus it is not the trimethylplatinum(IV) that is catalytically active. We considered the possibility that traces of boron triaryl generated in the salt metathesis reaction are the active catalyst. Surprisingly, a control experiment with 5% of commercially available $B(C_6F_5)_3$ led to 50% conversion within 5 min, but conversion slowed down and required 24 h to reach 84% conversion, which casts some doubt on the role of boron triaryls as catalysts in this reaction, in particular since previous ^{1}H NMR experiments showed that $[B(Ar^F)_4]$ was intact in the presence of oxygen-donating ligands during salt metathesis. Many apparently metal-catalyzed Mukaiyama reactions are in fact catalyzed by Lewis-acidic silicon species.[31] For example, Me_3SiOTf can act as a catalyst for the Mukaiyama-aldol reaction.[32] As a control, the same Mukaiyama−aldol reaction was run at room temperature in the presence of 5% pure Me_3SiOTf (Aldrich). After 2 h and 10 min, we observed 15% conversion to the aldolate, in an *anti:syn* ratio of 40:60. This ratio is the reverse of what Hollis and Bosnich[31a] observed in the same Me_3SiOTf-catalyzed reaction at −80 °C. After 24 h, the ^{1}H NMR revealed disappearance of the HC−OSi proton peaks of the aldolate and formation of byproducts, as indicated by the appearance of many peaks in the 1.0−2.5 ppm region. Clearly, our reactive mixture behaves differently than a reaction catalyzed by pure Me_3SiOTf. However, it is well-known that

(26) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1979**, *18*, 686.

(27) (a) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *J.Org. Chem.* **1993**, *58*, 1835. (b) Ohki, H.; Wada, M.; Akiba, K. *Tetrahedron Lett.* **1988**, *29*, 4719.

(28) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.

(29) Kobayashi, S.; Mori, Y.; Yamashita, Y. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. B., Eds.; Elsevier Pergamon: Amsterdam; Boston, 2004; Vol. 9.8, p 399.

(30) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Nayori, R. *J. Org. Chem.* **1983**, *48*, 932.

(31) (a) Hollis, T. K.; Bosnich, B. *J. Am. Chem. Soc.* **1995**, *117*, 4570. (b) Carreira, E. M.; Singer, R. A. *Tetrahedron Lett.* **1994**, *35*, 4323.

(32) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

Table 1. Comparison of Diastereoselectivities for the Mukaiyama-Type Aldol Reaction Between 1-Cyclohexenyl-OTMS and Benzaldehyde

catalyst	temp	*threo*/*erythro*	refs
5% Me_3PtOTf/ $Na[B(Ar^F)_4]$ (in situ)	RT	75/25 (CD_2Cl_2), 72/28 ($CDCl_3$)	this work
5% Me_3SiOTf	RT	40/60	this work
5% $B(C_6F_5)_3$	RT	73/27	this work
5% $I^-/BiCl_3$	RT	63/37	Dubac et al.[27a]
5% trityl perchlorate	−78 °C	36/64	Mukaiyama et al.[35]
10% Me_2AlCl	−78 °C	63/37	Yamamoto et al.[36]
100% (stoichiometric) $TiCl_4$	RT	77/23	Mukaiyama et al.[28]

the ligand attached to the "silyl cation" has crucial impact on the rate and outcome of the Mukaiyama-aldol reaction. For example, toluene-coordinated Et_3Si^+ is orders of magnitude more reactive than Me_3SiOTf.[33] The fact that many metal salts act as cocatalysts for Me_3SiOTf is well recognized.[31] The best hypothesis explaining our data seems to be that *in situ* $Na[B(Ar^F)_4]$ metathesis on $[\{Me_3PtOTf\}_4]$, in the presence of the silylated enol ether, generates trace amounts of extremely active, weakly ligated silyl cations. In this regard it is interesting to note that a very active cocatalyst was designed as a trap for triflate to activate the silyl cation.[34] Given the apparent propensity of triflate to coordinate to platinum(IV), it might be speculated that the platinum(IV) system acts by coordinating to triflate and thus activating silyl cations. From a practical point of view, the system described here works cleanly and within minutes at room temperature, and the good diastereoselectivity is fairly competitive with existing systems, as shown in Table 1.

Summary and Conclusion

We have shown that trimethylplatinum(IV) triflate exhibits moderate but significant Lewis-acidity, using Childs' crotonaldehyde method. A structure of an adduct between crotonaldehyde and trimethylplatinum triflate was obtained, where the structure was dimeric with bridging triflate. Although trimethylplatinum triflate can be used to generate highly electrophilic species, the intrinsic catalytic activity of the weakly ligated trimethylplatinum(IV)$^+$ unit was found to be commensurate with its Lewis-acidity, which is slightly below what is considered synthetically useful. However, ligand exchange was consistently found to be fast on the NMR time scale at room temperature, indicating that it is not slow ligand exchange that inhibits catalysis. The reason that $Me_3Pt(solv)_3^+$ systems are rather inefficient Lewis-acidic catalysts is thus rooted in the slightly too low intrinsic Lewis-acidity of the trimethylplatinum(IV) unit (27% of the acidity of BBr_3), a situation where the anticipated strong acidity of "Pt^{4+}" is attenuated by three strongly donating methyls. This platinum(IV) unit is thus on the "fast exchange, low Lewis-acidity" end of the spectrum. This strongly contrasts with the *trans*-$Pt(IV)Cl_4L_2$ systems, where extremely strong Lewis-acidity of the platinum(IV) centers enables unprecedented synthetically useful transformations at the ligands L (e.g., nitriles), albeit in a stoichiometric fashion because of the low substitution rate at chloride-ligated platinum(IV).[37] Now that the two extremes have been described, we think there exists a better basis for careful tuning of the electron density at the platinum(IV) center for the development of sufficiently strongly Lewis-acidic platinum(IV) systems that still exchange ligands fast enough to be of catalytic use.

Experimental Section

General Information. ^1H NMR spectra were collected on either a Varian Gemini 200 or Varian 500 spectometer in the solvents specified. The chemical shifts are reported in parts per million (δ), and the multiplicities are reported as s (singlet), d (doublet), (triplet), q (quartet), m (multiplet), and br (broad). All reactions were performed under inert conditions (water-free, oxygen-free) using J. Young NMR tubes. These tubes were oven-dried before use. Reactions were performed using dried glassware in a glovebox (N_2). CD_2Cl_2 and $CDCl_3$ obtained from Cambridge Isotopes were dried over CaH_2 and vacuum-transferred before use. Crotonaldehyde (95%), dimethyl maleate, pentamethylcyclopentadiene, trimethylsilyl trifluoromethanesulfonate (98%), benzaldehyde (99.5%), methacrolein (95%), isoprene (99%), 1-(trimethylsiloxy)cyclohexene (99%), and 1-bromo-2-chlorobenzene (99%) were obtained from Aldrich and stored over molecular sieves. $B(C_6F_5)_3$ (95%) was also purchased from Aldrich and stored in an inert atmosphere (N_2) glovebox. $Na[B(Ar^F)_4]$ was purchased from Matrix Scientific and dried under vacuum (0.02 Torr). $[\{Me_3PtOTf\}_4]$ was prepared according to published methods.[7,26] $[\{Me_3PtI\}_4]$ (99.8%) was purchased from Strem Chemicals.

Solution Data for Crotonaldehyde−Me_3PtOTf (Pt/aldehyde 1:1) Complex, [{$Me_3Pt(\eta^1$-O=CHCH=CHMe)(μ-OTf)}$_2$]: ^1H NMR (500 MHz, CD_2Cl_2) δ 9.46 (d, 1H, J = 8 Hz, CHO), 7.27 (dq, 1H, J = 16, 7 Hz, MeC*H*=CH), 6.38 (qdd, 1H, J = 1.5, 8, 16 Hz, MeCH=C*H*), 2.11 (dd, 3H, J = 1.5, 7 Hz, H_3C), 1.38 (s+d, 9H, $^2J_{PtH}$ = 80 Hz, Pt−Me); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 202.0 (C1), 163.5 (C3), 134.1 (C2), 20.0 (C4), −10.5 ($^1J_{PtC}$ = 813 Hz, Pt−Me).

Solution Data for Free Crotonaldehyde. ^1H NMR (500 MHz, CD_2Cl_2) δ 9.47 (d, 1H, J = 8 Hz, CHO), 6.87 (dq, 1H, J = 16, 7 Hz, MeC*H*=CH), 6.10 (qdd, 1H, J = 1.5, 8, 16 Hz, MeCH=C*H*), 2.06 (dd, 3H, J = 1.5, 7 Hz, H_3C); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 194.0 (C1), 154.4 (C3), 134.8 (C2), 18.7 (C4).

[Me_3Pt(O=CHCH=CHMe)$_3$]BF_4. $[\{Me_3PtI\}_4]$ (6.0 mg, 0.0163 mmol) and 4.05 μL (0.0489 mmol) of predominantly *trans*-crotonaldehyde were added to a J. Young NMR tube containing 522 μL of CD_2Cl_2. Under the exclusion of light, 3.17 mg (0.0163 mmol) of $AgBF_4$ was added, and reaction mixture was shaken for 30 s and left to react at room temperature. After 30 min AgI was removed by filtration, leaving a colorless solution. Solution data for $(CH_3)_3Pt(O{=}CHCH{=}CHMe)_3BF_4$: ^1H NMR (500 MHz, CD_2Cl_2) δ 9.40 (s br, 3H, C*H*O), 7.23 (s br, 3H, MeC*H*=CH), 6.28 (s br, 3H, MeCH=C*H*), 2.08 (s br, 9H, H_3C), 1.25 (s + d, ^2J(Pt,H) = 77.5 Hz, 9H, PtCH_3).

Crystal Structure of [{$Me_3Pt(\eta^1$-O=CHCH=CHMe)(μ-OTf)}$_2$]. Crystals were grown from a titration sample (see above), by keeping the sample at −35 °C for 5 months. $C_{16}H_{30}F_6O_8Pt_2S_2$, M_r = 918.70, orthorhombic, space group *Pccn*, a = 14.8158(3) Å, b = 17.7164(4) Å, c = 10.5482(3) Å; V = 2768.72(12) Å^3, Z = 4, ρ_{calc} = 2.204 g·cm^{-3}, Mo Kα radiation (λ = 0.71073 Å), crystal dimensions 0.12 × 0.10 × 0.06 mm^3. A total of 24 580 reflections were collected on a Nonius KappaCCD area detector at 150(2) K, of which 3163 were independent and 2387 were greater than 2σ-

(33) Hara, K.; Akiyama, R.; Sawamura, M. *Org. Lett.* **2005**, *7*, 5621.
(34) Oishi, M.; Aratake, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 8271.
(35) Mukaiyama, T.; Kobayashi, S.; Murakami, M. *Chem. Lett.* **1985**, 447.
(36) Naruse, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Chem. Lett.* **1985**, 1451.
(37) (a) Makarycheva-Mikhailova, A. V.; Kukushkin, V. Y.; Nazarov, A. A.; Garnovskii, D. A.; Pombeiro, A. J. L.; Haukka, M.; Keppler, B. K.; Galanski, M. *Inorg. Chem.* **2003**, *42*, 2805. (b) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.

(*I*). The structure was solved by direct methods and refined on F^2 using the SHELXTL (version 6.12) software package. Final residuals, R1 = 0.0403 ($I > 2\sigma(I)$), wR2 = 0.1020 (all data). Further details of the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC 286 403.

Diels−Alder Reactions. Cp*H + dimethyl maleate + 5% Pt in the form of [{Me_3PtOTf}$_4$]. Under inert conditions, 12.5 μL (0.1 mmol) of dimethyl maleate, 16 μL (0.1 mmol) of Cp*H, and 2.0 mg (0.5×10^{-2} mmol Pt) of [{Me_3PtOTf}$_4$] were added to a J. Young NMR tube containing 550 μL of CD_2Cl_2, 11.7 μL (0.1 mmol) of 1-bromo-2-chlorobenzene, and a small amount of TMS. ^{1}H NMR of the *anti-endo* adduct formed: (500 MHz, CD_2Cl_2) δ 3.6 (s, 6H, H_3C−OOC), 3.0 (s, 2H, C*H*COOMe), 1.6 (s, 6H, H_3C−C═C−CH_3), 1.4 (q, 1H, H_3CC*H*), 1.1 (s, 6H, H_3C−CCHMe), 0.6 (d, 3H, H_3CCH).

NOE Confirmation of *anti-endo* Geometry. Irradiation of the C*H*COOMe resonance led to observation of an NOE at H_3CC*H* but not at H_3CCH. Irradiation of the H_3CC═CCH_3 resonance led to observation of an NOE at H_3C−OOC but not at C*H*COOMe. Irradiation of the H_3CC*H* resonance led to the observation of an NOE at C*H*COOMe but not at H_3C−OOC.

Cp*H and [{Me_3PtOTf}$_4$] 1:1 Mixture. Under inert conditions, 8 μL (0.05 mmol) of Cp*H and 19.5 mg (0.05 mmol) of Pt in the form of [{Me_3PtOTf}$_4$] were added to a J. Young NMR tube containing dry CD_2Cl_2. Cp*PtMe$_2$(OTf): ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.77 (s, 15 H, {η^5-C$_5$(CH_3)$_5$}, $^3J_{Pt-H}$ = 22 Hz), 1.43 (s, 6H, 2{CH_3}, $^2J_{Pt-H}$ = 70 Hz).

[{Me_3PtOTf}$_4$]-Catalyzed Reaction between Isoprene and Methacrolein. Under inert conditions, 8 μL (0.1mmol) of methacrolein, 2.0 mg (5 μmol Pt) of [{Me_3PtOTf}$_4$], and 10. μL (0.1 mmol) of isoprene were added to a J. Young NMR tube containing dry $CDCl_3$, and the reaction proceeded as described under Results and Discussion above. The 1,4-adduct is obtained; 1,4-dimethylcyclohex-3-enecarbaldehyde: ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.47 (s, 1H, C*H*O), 5.37 (m, 1H, *H*C═C), 2.35−1.79 (m, 6H, H_2C═CH, H_2CCH$_2$, H_2CC(Me)═CH), 1.53 (m, 3H, H_3CC═CH), 1.04 (s, 3H, H_3CCCHO).

Generation of B(Ar^F)$_3$ from NaB(Ar^F)$_4$ and [{Me_3PtOTf}$_4$]. To a solution containing 520 μL of C_6D_6 and 1.9 mg of [{Me_3PtOTf}$_4$] (4.9 μmol of Pt) was added 4.0 mg (4.5 μmol) of NaB(Ar^F)$_4$. Both reagents dissolved, and upon shaking, the colorless solution darkened to a light amber color. NaOTf precipitated within minutes, as white microcrystals. The solution, which had slightly darkened upon mixing, turned brownish-orange within minutes and continued to darken over a period of a few hours, as black precipitate started to form. The solution was filtered, and the filtrate volume was reduced, from which white crystals were grown. Determination of the unit cell constants by single-crystal X-ray diffraction identified the compound as the known B(Ar^F)$_3$.

Mukaiyama-Aldol Reactions. [{Me_3PtOTf}$_4$] + Na[B(Ar^F)$_4$] catalyzed Mukaiyama-aldol reaction: Under inert conditions, 10 μL (0.1 mmol) of benzaldehyde and 19.5 μL (0.1 mmol) of 1-cyclohexenyl-OTMS were added to a J. Young NMR tube containing 520 μL of CD_2Cl_2 and 2.0 μL (25 μmol) of 1,2-dichloroethane as an internal standard. Then 4.43 mg (5 μmol) of Na[B(Ar^F)$_4$] was completely dissolved in the solution, and finally 2.0 mg (5 μmol of Pt) of [{Me_3PtOTf}$_4$] was added to the mixture. The NMR tube was shaken for approximately 30 s, after which a cloudy white precipitate appeared and remained suspended in the solution. The reaction was complete when the first NMR spectrum was acquired (within 5 min), and the product ratio was determined from ^{1}H NMR integration. Yield was quantitative. Removal of CD_2Cl_2 and vacuum transfer of $CDCl_3$ allowed for direct comparison with literature[27] data: ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.06 (*anti*) and 0.00 (*syn*) (9H, 2s, *anti*:*syn*, 75:25), 1.22−2.66 (6 H, m), 2.10−2.45 (3 H, m), 5.02 (*anti*) and 5.27 (*syn*) (1 H, 2d, *anti*:*syn*, 75:25, J = 8 Hz and J = 4 Hz, respectively). A product ratio *anti*:*syn* = 72:28 was obtained when the reaction was performed in $CDCl_3$ in quantitative yield.

5% Me_3SiOTf Catalysis of the Mukaiyama-Aldol Reaction. Benzaldehyde (10.1 μL, 0.1 mmol) and 19.5 μL (0.1 mmol) of 1-cyclohexenyl-OTMS were added to a J. Young NMR tube containing 522 μL of CD_2Cl_2. Then 0.91 μL of Me_3SiOTf (99% Sigma-Aldrich) was added, and 1.97 μL (2.5×10^{-2} mmol) of 1,2-dichloroethane was also added, as internal standard.

Synthesis of [$Me_3Pt(benzaldehyde)_3$]BF$_4$. [{Me_3PtI}$_4$] (6.0 mg, 0.0163 mmol) and 5.0 μL (0.0489 mmol) of benzaldehyde were added to a J. Young NMR tube containing 522 μL of CD_2Cl_2. Under the exclusion of light, 3.17 mg (0.0163 mmol) of $AgBF_4$ was added, and the reaction mixture was shaken for 30 s and left to react at room temperature. After 30 min AgI was removed by filtration, leaving a colorless solution. Solution data for $(CH_3)_3Pt(C_6H_5CHO)_3BF_4$: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 10.015 (s, 3H, C*H*O), 7.99 (d, J(H,H) = 7 Hz, 6H, C−H), 7.75 (t, J(H,H) = 7.4 Hz, 3H, C−H), 7.55 (t, J(H,H) = 7 Hz, 6H, C−H), 1.55 (s + d, ^2J(Pt,H) = 73.0 Hz, 9H, PtCH_3).

Testing $Me_3Pt(benzaldehyde)_3BF_4$ for Activity in the Mukaiyama-Aldol Reaction. Benzaldehyde (10 μL, 0.1 mmol) and 19.5 μL (0.1 mmol) of 1-cyclohexenyl-OTMS were added to a J. Young NMR tube containing 480 μL of CD_2Cl_2, 2.0 μL (2.5×10^{-2} mmol) of 1,2-dichloroethane as an internal standard, and 5% mol of $(CH_3)_3Pt(benzaldehyde)_3BF_4$ (prepared as described above). The reaction was monitored by NMR spectroscopy. Catalysis to yield Mukaiyama products was not observed, and decomposition products appeared slowly (within 24 h).

Borane-Catalyzed Mukaiyama-Aldol Reactions. Benzaldehyde (10 μL, 0.1 mmol) and 19.5 μL (0.1 mmol) of 1-cyclohexenyl-OTMS were added to a J. Young NMR tube containing 520 μL of $CDCl_3$ and 2.0 μL (25 μmol) of 1,2-dichloroethane as an internal standard. Then 2.6 mg (5 μmol) of B(C$_6$F$_5$)$_3$ was then added to the solution. The NMR tube was shaken for approximately 30 s and monitored by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.26 (*anti*) and 0.26 (*syn*) (9H, 2s, *anti*:*syn*, 75:25), 1.55−2.55 (6 H, m), 2.30−2.74 (3 H, m), 5.02 (*anti*) and 5.27 (*syn*) (1 H, 2d, *anti*:*syn*, 75:25, J = 8 Hz and J = 4 Hz, respectively).

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Supporting Information Available: X-ray crystallographic data for [{Me_3Pt(crotonaldehyde)(μ-OTf)}$_2$] (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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