Multidimensional ^{109}Ag, ^{31}P, and ^{1}H HMQC and HSQC NMR Studies on a Model Homogeneous Catalyst. Reactions of a Chiral Ferrocenylphosphine with Ag(CF_3SO_3)

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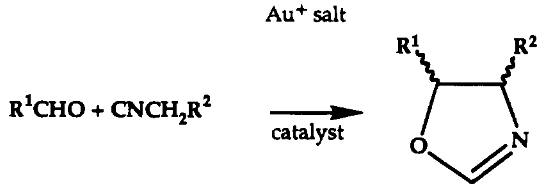
The chiral ferrocene ligand Fe{1-(PPh_2)-2-((*R*)-CH(Me)N(Me)$CH_2CH_2NMe_2$)C_5H_3}{$C_5H_4PPh_2$}, **1**, reacts with Ag(CF_3SO_3) to form a trinuclear complex $Ag_3(\mathbf{1})_2(CF_3SO_3)_3$, **3**, in which there are two different silver coordination spheres. In one environment two silver cations complex to the 1-PPh_2 P atom and the two N atoms of the side chain, from two ligands **1**, whereas the third silver cation coordinates to two P atoms from two $C_5H_4PPh_2$ moieties. Reaction of **3** with a 70-fold excess of the isonitrile $CNCH_2CO_2Me$, **4**, affords a mononuclear complex, **5**, in which both P atoms of **1** chelate to silver(I). The number of coordinated ^{31}P spins for **3** and **5** and the coordination of the chiral side chain in **3** were determined using HSQC and HMQC ^{109}Ag−^{31}P, ^{109}Ag−^{1}H, and ^{31}P−^{1}H multidimensional methods. The relevance of these observations to the Au(I)-catalyzed aldol condensation of aldehydes with isonitriles is discussed.

Introduction

The reaction of isocyanides with aldehydes to form dihydrooxazoles can be catalyzed by gold(I) salts,[1,2] as shown in eq 1. If the reaction is carried out in the presence of a chiral auxiliary, such as **1**, the organic products show substantial enantiomeric excesses.[1,2] Mechanistically, the reaction is presumed to proceed through an intermediate complex in which the coordination sphere is composed of the metal, the two phosphorus donors of **1**, and at least one isonitrile molecule, although this structure has not been proven. After the isonitrile is deprotonated by a suitable base, its enolate form is attacked by the aldehyde to form product(s). For **1**, the base is provided by the chiral side chain.



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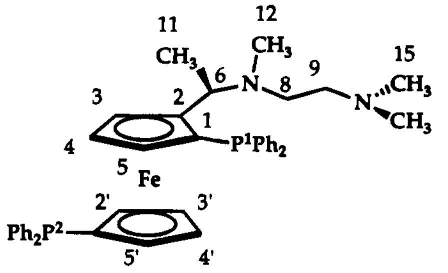
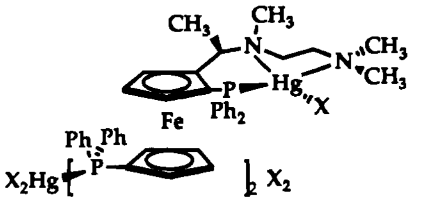


1

Model studies using mercury(II) halide complexes,[3] together with **1**, led to the isolation and characterization of trinuclear complexes of type **2**. These compounds contain two mercury atoms each with a coordinated tridentate and one mercury center with two monodentate tertiary phosphine donors. This coordination sphere was identified using ^{199}Hg NMR together with ^{31}P−^{1}H heteronuclear multiple-quantum correlation (HMQC) spectroscopy. It was concluded[3] that the complex chemistry of **2** involved coordination of the nitrogen side chain. The mercury complexes did not show catalytic activity[3] related to the chemistry of eq 1.



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Hayashi and co-workers[4] have also reported an NMR study for a silver(I) complex whose behavior is thought to be related to the catalytic chemistry of gold(I). We offer here new HMQC ^{109}Ag and ^{31}P multidimensional NMR results which help to clarify the behavior of **1** with Ag(CF_3SO_3) in the absence of and in the presence of an excess of isonitrile.

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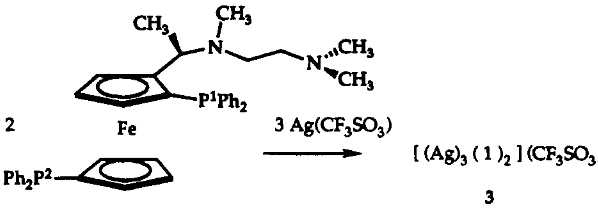
Results and Discussion

The reaction of **1** with silver(I) triflate, as shown in eq 2, gives an isolable yellow-brown complex in good yield. The



(2)

2:3 ratio of **1**:Ag(CF_3SO_3) was chosen on the basis of the results for the mercury chemistry (a 1:1 ratio gives mostly **3**, as determined by low-temperature NMR).

Complex **3** gave a satisfactory microanalysis and a weak set of peaks in its FAB mass spectrum at *m*/*e* = 1986.6 (<1% of base), which corresponds to $[[Ag_3(\mathbf{1})_2](CF_3SO_3)_2]^+$. There is a relatively strong set of signals at *m*/*e* = 789 ($Ag(\mathbf{1})^+$; 50% of base) and at *m*/*e* = 1046.9 ($Ag_2(\mathbf{1})(CF_3SO_3)^+$; 16.3%). There is also a weak set of signals, comparable in intensity to those at *m*/*e* 1986.6 surrounding *m*/*e* = 2245, and these would fit for $[[Ag_4(\mathbf{1})_2](CF_3SO_3)_3]^+$.

The ^{31}P NMR spectrum of **3** is broad at ambient temperature; however, at 253 K it shows two types of phosphorus in the ratio 1:1. The high-frequency absorption, $\delta = +2.5$, has a one-bond coupling constant, $^1J(^{109}Ag,^{31}P) = 560$ Hz, whereas the low-frequency signal, $\delta = -4.5$, shows a substantially larger coupling constant, $^1J(^{109}Ag,^{31}P) = 749$ Hz. The former is consistent with, but the latter value too large for, a simple "$AgP_2{}^+$" type coordination sphere.[5] However, this large value is reminiscent of the unexpectedly large $^1J(^{199}Hg,^{31}P)$ values, ca. 5000–7500 Hz, found[3] for **2** (X = Cl, Br, I), where the mercury atom has only one coordinated ^{31}P spin, one halogen ligand, and two bound N atoms from the side chain. $^1J(^{109}Ag,^{31}P)$ values of the order of 800 Hz are known[6] but are usually associated with a phosphorus ligand having strongly electronegative substituents, $P(OMe)_3$ or $P(NMe_2)_3$.[5,6] Interestingly, relatively large values of 712 and 759 Hz have been reported for $Ag(PEt_3)BF_4$ and $Ag(PBu^n{}_3)BF_4$, respectively.[6a] Further, van Koten and co-workers[6c] find $^1J(^{109}Ag,^{31}P) = 650$ Hz for $(Ph_3PAg)_4(O_4C_{12}H_6)_2$, a molecule with one ^{31}P spin per Ag atom. These complexes all contain just one coordinated tertiary phosphine. It is worth noting that we do not observe two-bond $^2J(^{31}P,^{31}P)$ coupling.

A ^{31}P–^1H heteronuclear multiple-quantum coherence[7–9] (HMQC) spectrum (see Figure 1) indicates that the low-frequency ^{31}P resonance couples not only to some of its Cp protons but also to several of the protons arising from the side chain. Specifically, one finds interactions with one of the two geminal NMe_2 methyls and also with the single NMe. The other ^{31}P nucleus interacts only with several of its Cp protons. This supports the hypothesis based on the $^1J(^{109}Ag,^{31}P)$ values that we have one Ag environment with one coordinated phosphorus (together with the nitrogen side chain) and one Ag with two coordinated phosphorus ligands.

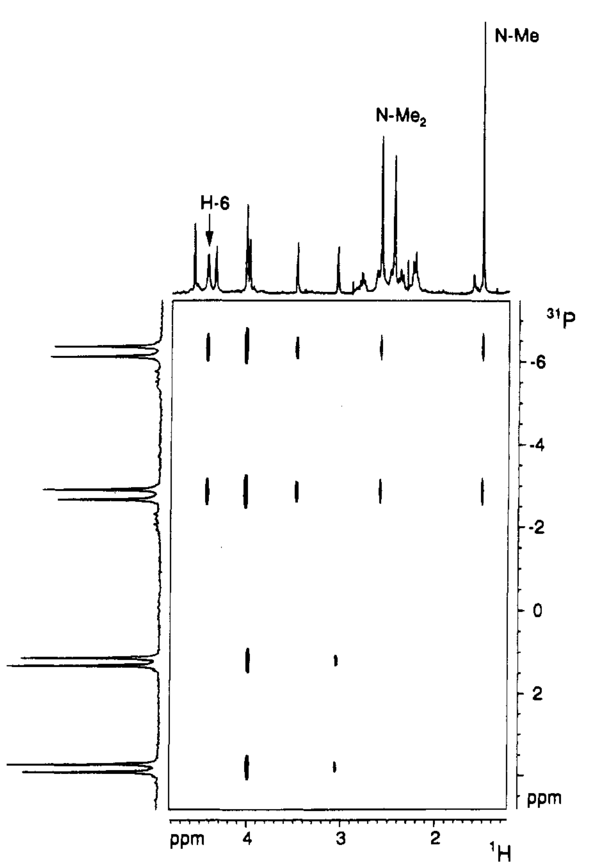
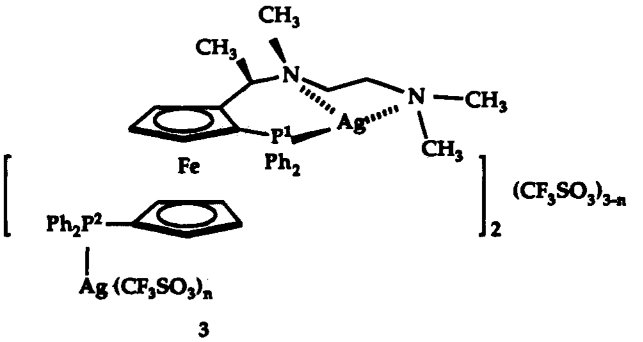


Figure 1. ^{31}P–^1H correlation for **3** showing that the low-frequency ^{31}P absorption correlates to Cp and side-chain protons, whereas the high-frequency ^{31}P absorption correlates only to two Cp protons (CD_2Cl_2, 253 K, 500 MHz).

The situation for **3** becomes clear upon inspection of both the ^{109}Ag–^{31}P HSQC (at ambient temperaure) and the ^{109}Ag–^1H HMQC (at 253 K) spectra. The former reveals two different ^{109}Ag absorptions, $\delta = 690$ and $\delta = 540$, with 1:0:1 multiplicity due to **two** partners plus a doublet from a single ^{31}P partner (see Figure 2). The latter shows that the ^{109}Ag signal at $\delta = 540$ is spin–spin coupled to several of the protons from the **nitrogen side chain**. Taken together, all the NMR data point to a structure for **3** that is related to that for **2**, with a reasonable choice being



3

Our results are consistent with relatively robust Ag–P and Ag–N bonds for the monophosphine–silver moiety but relatively labile Ag–P bonds for the diphosphine–silver complex. Among other things, **3** explains why one does not observe a $^2J(^{31}P,^{31}P)$ value, in that the nonequivalent ^{31}P spins reside on

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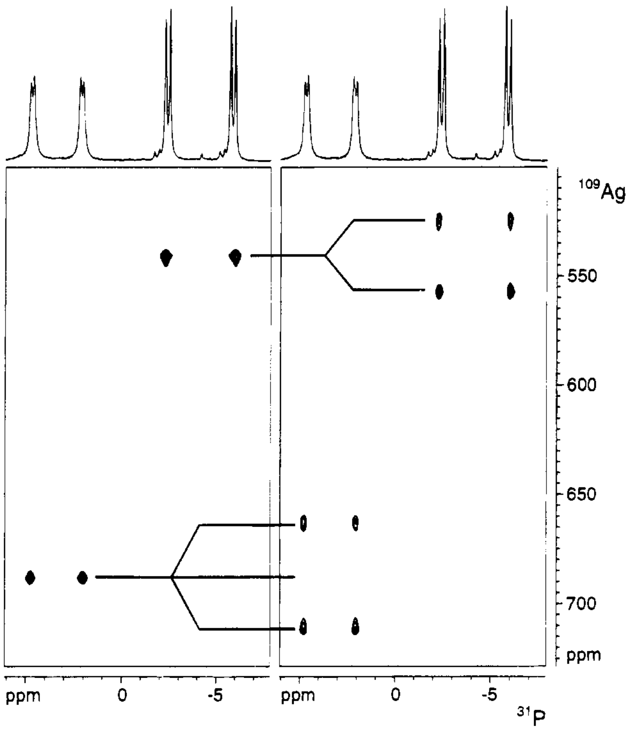
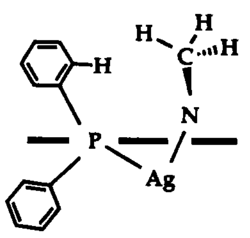


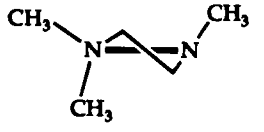
Figure 2. ^{109}Ag−^{31}P HSQC correlations with inverse detection revealing two different ^{109}Ag resonances. The spectrum on the left was obtained using an additional decoupling pulse in the middle of the evolution period. The separation of the cross peaks in the spectrum on the right for the high-frequency ^{109}Ag signal corresponds to twice the observed $^{1}J(^{109}\text{Ag},^{31}\text{P})$ coupling and indicates the presence of two ^{31}P spins on this metal spin (CD_2Cl_2, 253 K, 202 MHz).

different metal centers. We cannot be certain of the number of coordinated triflate ligands and note, again, that the complex is dynamic on the NMR time scale. The $^{1}J(^{109}\text{Ag},^{31}\text{P})$ value of 560 Hz is consistent with a metal center which is two-coordinate, based on various NMR reports concerned with this coupling constant.[10−12] It is worth noting that there are not many examples of HMQC two-dimensional methods involving ^{109}Ag[8,13,14] and, in general for metals, few[15] using ^{31}P as the source of the polarization, i.e., HSQC ^{109}Ag−^{31}P spectroscopy. Silver-109 NMR spectroscopy was reviewed recently,[16] but there is still only a sparce literature on this subject.

A 2-D ^{1}H NOESY spectrum for **3** reveals further subtle detail. Specifically, the configuration at N-7 is *S* on the basis of an NOE from CH_3-11 to an ortho proton of one of the P^1 phenyl rings; i.e., the CH_3-11 is above the C-1−C-5 Cp ring. The ortho proton showing this NOE has been identified as being in the phenyl ring shown:



Two further points concerned with the two $N(CH_3)_2$ resonances: (a) there is no NOE from CH_3-11 and (b) there is no NOE from the P^1 phenyl protons. We interpret point (a) as being consistent with the conformation



(view from behind the CH_2−CH_2 bridge toward the silver atom) and point (b) to suggest a flat (trigonal) silver for the Ag^+ coordinated to the side chain. If the Ag^+ were to be tetrahedral (or pseudotetrahedral), this would bring the PPh protons well within range for an NOE to the $N(CH_3)_2$ methyl groups.

Variable-temperature ^{31}P NMR studies on samples of **3**, containing 1−3 equiv of the isonitrile ligand $CNCH_2(CO_2Me)$, **4**, revealed the presence of several complexes; moreover, there are at least two dynamic processes proceeding simultaneously. The most informative NMR spectra came from a CD_2Cl_2 solution of **3** in the presence of a ca. 70-fold excess of **4**. A single complex, **5**, is formed. The 202 MHz ^{31}P spectrum at 233 K suggested that the two different ^{31}P absorptions had almost identical chemical shifts, $\delta = -5.5$, and almost identical $^{1}J(^{109}\text{Ag},^{31}\text{P})$ values (ca. 345 Hz). The ^{109}Ag−^{31}P HSQC spectrum at 233 K (Figure 3) revealed a single silver resonance, $\delta = 1374$, and confirmed that **two** ^{31}P spins were coordinated. Clearly, the presence of the excess isonitrile results in breakdown of the trinuclear complex **3** and formation of a mononuclear compound.

The much smaller $^{1}J(^{109}\text{Ag},^{31}\text{P})$ for the new complex **5** suggests coordinated isonitrile, and it remains to decide whether

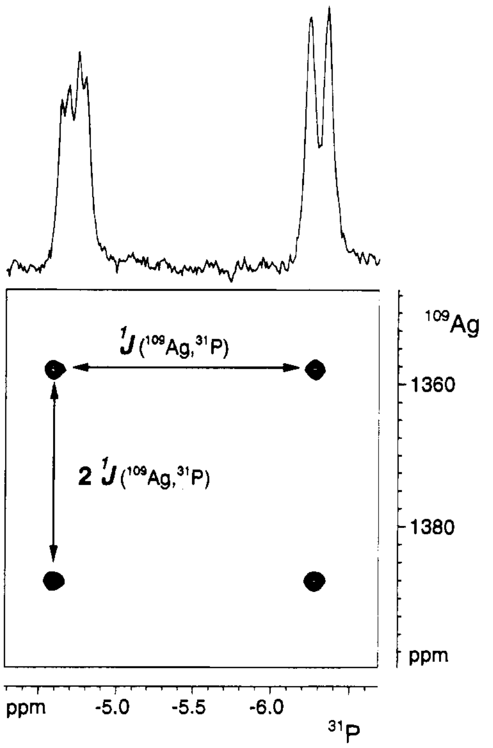


Figure 3. ^{109}Ag−^{31}P HSQC correlation with inverse detection revealing one metal resonance. The separation in the metal direction corresponds to twice the observed $^{1}J(^{109}\text{Ag},^{31}\text{P})$ value, once again indicating two coordinated phosphine ligands (CD_2Cl_2, 233 K, 202 MHz). Note that the ^{31}P chemical shifts are almost identical, so that only the more intense signals of the AB subspectra are observed.

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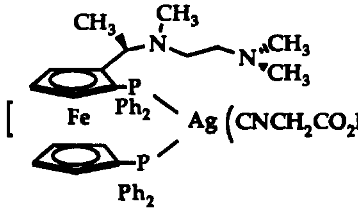
there are one or two molecules of **4** bound to the Ag atom. FAB mass spectroscopy on the solution used for the NMR measurements containing the 70-fold excess showed a weak, but readily detectable, signal at *m*/*e* = 990.9, consistent with the formulation $[Ag(\mathbf{1})(\mathbf{4})_2](CF_3SO_3)$, i.e. two bound isonitriles, as shown in structure **5**. An attempt at infrared analysis on the solution with 70-fold excess was inconclusive.



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We have isolated a complex from the solution with a 3-fold excess of **4** by adding a methanolic solution of $NaBPh_4$ and collecting the precipitate which results. The microanalytical data for this material are not satisfactory in carbon but, on the basis of the nitrogen analysis, clearly show that only **one** isonitrile is present. One might choose to argue for a three-coordinate complex with the coordination sphere "$Ag(\mathbf{4})P_2{}^+$" on the basis of the empirical observations by Muetterties and Alegranti[10] concerned with $^1J(^{109}Ag,^{31}P)$ and coordination number, i.e. that 345 Hz seems large for a four-coordinate Ag(I); however, there is much danger in drawing conclusions based on poor models, so that we must accept that we are not certain of the number of complexed isonitriles. Hayashi et al.,[17] in related chemistry, report an equilibrium between three- and four-coordinated complexes of the type $[Ag(\mathbf{4})P_2]^+$ and $[Ag(\mathbf{4})_2P_2\}^+$ with the observation that the three-coordinate is favored at higher temperature, so that perhaps both of our observations, i.e., three-coordinate isolated but four-coordinate in the 70-fold excess case, are correct.

Comment. Although the exact nature of the coordination sphere for **5** is not clear, we can say with certainty that both ^{31}P spins are coordinated to a single silver cation and, consequently, that the mechanistic proposal put forth by Hayashi[1] for the Au(I)-catalyzed aldol-type reaction is reasonable. It would seem that a trinuclear silver (and Hg(II)[3]) species is favored in the absence of the isonitrile but that this collapses to a mononuclear silver complex in the presence of a substantial excess of isonitrile. For both **3** and **5** we do not know what role, if any, is played by the triflate anions; indeed, from our NMR studies, we cannot say whether any are coordinated.[18] It is interesting that **3** forms predominantly as a single diastereomer.

Experimental Section

FAB mass spectroscopy and microanalytical measurements were performed in the analytical laboratories of the ETH-Zentrum.

NMR Spectroscopy. One-dimensional ^1H and $^{31}P\{^1H\}$ NMR spectra were measured on Bruker AC 250 and AMX 500 spectrometers at 250.13 (500.13) and 101.3 (202.5) MHz, respectively. Referencing is relative to internal TMS and external 85% H_3PO_4 and $AgClO_4$ extrapolated to infinite dilution for ^1H, ^{31}P, and ^{109}Ag, respectively. Two-dimensional NOESY, with a mixing time of 800 ms, and $^{31}P-^1H$ correlation spectra were measured as described by us[19] before. $^{109}Ag-^1H$ heteronuclear multiple quantum coherence spectra were recorded with ^1H detection at 500.13 MHz using the pulse sequence $\pi/2\ (^1H)-\Delta-\pi/2\ (^{109}Ag)-t_1/2-\pi\ (^1H)-t_1/2-\pi/2\ (^{109}Ag)$–acquisition ($^1H$), where Δ had been set to 100 ms. $^{109}Ag-^{31}P\ \{^1H\}$ heteronuclear single quantum coherence spectra were measured using the pulse sequence $\pi/2\ (^{31}P)-\Delta-\pi\ (^{31}P)/\pi\ (^{109}Ag)-\Delta-\pi/2\ (^{31}P)/\pi/2\ (^{109}Ag)-t_1/2-\pi\ (^{31}P)-t_1/2-\pi/2\ (^{31}P)/\pi/2\ (^{109}Ag)$–acquisition ($^{31}P$) and continuous broad-band ^1H decoupling with the WALTZ-16 sequence. Δ was set to 0.34 ms. The multiplicity of the Ag resonance with respect to the ^{31}P spins was determined using the non-refocussed version of the above pulse scheme where the π (^{31}P) pulse in the middle of the t_1 evolution period had been omitted.

$[Ag_3(1)_2](OTf)_3$ (3). **1** (1 g, 1.46 mmol) was dissolved in 2.5 mL of methylene chloride. A solution of AgOTf (0.564 g, 2.20 mmol) in 2.5 mL of methylene chloride was slowly added. The resulting solution was stirred for 90 min. The solvent was removed under reduced pressure and the resulting solid extracted three times with toluene (50, 30, and 20 mL). The toluene was removed under reduced pressure to afford 1.15 g of product (75% yield). Anal. Calcd (found) for $C_{85}H_{88}Ag_3F_9Fe_3N_4O_9P_4S_3$: C, 47.80 (48.37); H, 4.15 (4.53); N, 2.62 (2.23). $\delta(^1H)$: H-3, 4.12; H-4, 4.61; H-5, 3.56; H-6, 4.48; CH_3-11, 0.88; NCH_3-12, 1.53; $N(CH_3)_2$, 2.46, 2.60

Reaction of 3 with $CNCH_2CO_2Me$. **3** (50 mg, 0.023 mmol) was dissolved in 1 mL of CD_2Cl_2. A 2.1-μL portion (0.023 mmol) of $CNCH_2CO_2Me$ was added. Three additional samples were prepared in an identical fashion with the exception of adding 4.2, 6.3, and 147 μL excesses of $CNCH_2CO_2Me$. For all samples the phosphorus-31 spectra were recorded at different temperatures (293, 273, 253, 233, 213, and 193 K).

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(18) For both 3 and 5 we have measured ^{19}F spectra from 203 to 273 K. Throughout this temperature range there is only one signal in both cases. At 253 K for **3** $\delta = -78.6$ and for **5** $\delta = -79.5$, relative to $CFCl_3$. "Coordinated" CF_3SO_3 has been reported by us[20] at $\delta = -76.9$ in a Pd(I) dimer. Venanzi and co-workers[21,22] report $\delta = -78.56$ and $\delta = -78.24$ for **both coordinated and noncoordinated CF_3SO_3**, respectively, in one ruthenium complex and then $\delta = -76.76$ and $\delta = -78.51$ for **both noncoordinated and coordinated CF_3SO_3**, respectively, in a second different ruthenium complex ($AgCF_3SO_3$ in CD_3CN, $\delta = -75.50$). We note from these data that uncoordinated triflate shows ^{19}F signals close to those we report above and that the signal can change position by several ppm and still be uncoordinated. We do not believe our ^{19}F chemical shifts to be of analytical value, apart from showing that we most likely have an equilibrium between complexed and noncomplexed triflate which averages the ^{19}F positions.

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