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Empirical Estimation of the Molecular Weight of Gold Complexes in Solution by Pulsed-Field Gradient NMR

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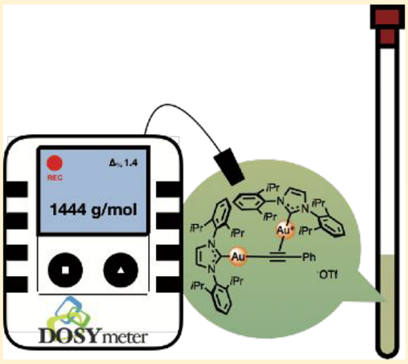
Supporting Information

ABSTRACT: Homogenous gold catalysis has emerged as a powerful tool in organic synthesis, but many mechanistic questions in that area remain unanswered. The ability of diffusion-ordered NMR spectroscopy (DOSY) to investigate interactions between substrates, to study molecular assemblies, and to characterize reactive intermediates makes it a powerful technique to get a better understanding of gold-catalyzed processes. In this article, we show that a simple empirical approach makes it possible to derive estimates of the molecular weight of gold complexes from their translational diffusion coefficients measured with DOSY. This approach is based on external calibration curves (ECC), modified to take into account the molecular density of gold complexes. The estimated molecular weights in turn provide information on interactions, as notably illustrated here with ion pairing, and have the potential to provide key information to rationalize the reactivity of reagents in gold-catalyzed reactions.



INTRODUCTION

Over the past 18 years, gold catalysis has opened new perspectives in organic chemistry and has played a key role in the synthesis of complex molecules from simple precursors.[1−17] While gold(I) and gold(III) complexes have been considered to be inert for a long time, a tremendous number of studies now clearly demonstrate the great interest of gold derivatives in homogeneous catalysis. This synthetic work has been supported by coordination chemistry efforts, which have identified various families of neutral or cationic mono- or digold complexes that are now broadly applied and easily available from commercial sources. One of the most salient features of gold complexes is their ability to activate CC π bonds (alkynes, alkenes, or allenes) toward nucleophilic attack. This means that the coordination of a soft CC π bond to a soft gold-based Lewis acid renders the LUMO of the substrate, such as an alkyne, more accessible to the HOMO of a variety of nucleophiles. However, the choice of ligands, counterions, solvents, and other experimental parameters is still a tedious task. Although high levels of selectivity are usually observed, anticipation and rationalization of the outcome of gold-catalyzed reactions also remain challenging. To gain deeper insight into gold-catalyzed transformations, intensive mechanistic work has been provided. On several occasions, it has been shown that the mechanisms are more complex than originally thought. For instance, it is now clearly established that the counterions of cationic gold catalysts can have a dramatic influence on the selectivity[13] or that some reactions actually require several catalyst molecules to activate the substrates. In this context, the arsenal of spectroscopy and spectrometry techniques at the chemists' disposal to analyze the mechanisms of gold-catalyzed transformations without affecting the catalytic process is still incomplete.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful method for the noninvasive analysis of molecules in solution. Pulsed-field gradient (PFG) NMR and its implementation DOSY (for diffusion-ordered NMR spectroscopy)[18] are a particularly relevant approach for the analysis of organometallic compounds in solution. DOSY provides, for each peak in an NMR spectrum, an estimate of the translational diffusion coefficients of the corresponding molecules. For the interpretation of these coefficients, several techniques are available that provide information on molecular sizes and shapes.[19−21] Typically, the Stokes−Einstein equation,[22] or a derivative thereof, is used to estimate hydrodynamic radii, and this approach has proven to be very successful for the analysis of organometallic compounds with, for example, the characterization of ion pairs.[23−25] For gold complexes, recent examples include the analysis of the bonding mode of cationic gold(I) species in solution[26] and

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the study of counterion effects.[27] Alternatively, empirical relationships can be established to obtain estimates of molecular weights from measured diffusion coefficients. Such relationships may also be derived from the Stokes−Einstein equation.[28,29] More accurate results are usually obtained with power laws of the form $D = K\mathrm{MW}^{\alpha}$,[30] where K and α are coefficients that are specific to a given class of compounds and require a calibration.[31−33] A first option is to derive an internal calibration curve (ICC) by including multiple reference molecules in the sample.[31,33] Applications of this approach have given information on the aggregation state of organolithium complexes in solution[31,34] and their degree of solvation.[35] Recently, Stalke and co-workers have proposed to replace the use of multiple internal references by a single internal reference, which may be the solvent, used together with external calibration curves.[36−39] The use of a reference and a normalization step makes it possible to derive calibration curves that are largely independent of the reference, temperature, and other experimental parameters. Applications of the ECC approach have been reported in organolithium chemistry to provide a reliable and straightforward indication of the aggregation state of lithium diisopropylamide in hydrocarbon solvents.[40] The validity of a given calibration curve, however, is still restricted to specific classes of compounds.

In this article, we show that important pieces of information on the interaction between cationic gold(I) complexes and their counterion or the substrate can be obtained using pulsed-field gradient NMR, together with external calibration curves (ECC). The accuracy of the ECC approach is highly dependent on the choice of model parameters, and new ECCs are derived here using a set of gold-containing compounds. These relationships are then used to estimate the molecular weights of gold complexes in solution from their diffusion coefficients. With the example of several cationic gold catalysts, we show that PFG NMR with ECC gives information on the type of ion pairing in solution with no need to observe the counterion by NMR. The interactions of gold complexes with several alkynes are also analyzed.

■ RESULTS AND DISCUSSION

As mentioned above, external calibration curves have been shown to be applicable for a specific range of molecular density, where the molecular density can be defined as the ratio of the molecular weight over the sum of the van der Waals volume of the atoms in the molecule.[36] Existing calibration curves were derived from molecules composed of carbon, hydrogen, and heteroatoms of the third period, with molecular densities in the (4−6) × 10^{29} g/(mol·m^3) range. Unsurprisingly, when these calibration curves were applied to gold complexes, large systematic errors were obtained. For example, for the (JohnPhos)AuCl complex, which is widely used in gold catalysis, with the existing ECC for dichloromethane solutions, the estimated molecular weight was 442 g/mol, while the correct value is 531 g/mol, corresponding to a relative error of 20.1%. With a van der Waals radius of 166 pm and an atomic weight of 196 g/mol, the gold atom has a molecular density of 1.03 × 10^{31} g/(mol·m^3), far outside the range covered by existing calibration curves.

In order to assess the possibility to establish an empirical relationship between the molecular weight and normalized diffusion coefficient that would be applicable to gold catalysts, a series of DOSY experiments was carried out on a selection of 13 di- and monogold complexes, as listed in Table 1. For this study, the experiments were performed in deuterated dichloromethane, which is a very common solvent in gold catalysis. The use of external calibration curves requires a single internal standard. Common choices for the internal standard include the residual, partially undeuterated solvent as well as relatively inert molecules such as adamantane, cyclopentane, tetramethylsilane, and naphthalene. Here, in order to establish the external calibration curves, the measured diffusion coefficients were normalized against adamantane. The fixed values of the diffusion coefficient of the reference ($D_{\mathrm{ref,fix}}$) were estimated by using the average log D value of 13 DOSY measurements of 33 mM solution at 25 °C (Table 2).

Table 1. Gold Complexes Used to Derive External Calibration Curves[a]

	complex[b]	MD g/(mol·m^3)	MW (g/mol)
a	$(\mathrm{Et_3P})\mathrm{AuCl}$	1.28 × 10^{30}	350
b	$(t\mathrm{Bu_3P})\mathrm{AuCl}$	9.38 × 10^{29}	434
c	$(\mathrm{Ph_3P})\mathrm{AuCl}$	9.51 × 10^{29}	494
d	(IPr)AuCl	7.49 × 10^{29}	621
e	(phosphite)AuCl	6.63 × 10^{29}	879
f	(CDP)AuCl	7.51 × 10^{29}	769
g	(IPr)AuOH	7.29 × 10^{29}	602
h	(R,R)-(DIOP)-$(\mathrm{AuCl})_2$	9.85 × 10^{29}	963
i	(CDP)-$(\mathrm{AuCl})_2$	9.44 × 10^{29}	1001
j	(R)-(DM-SEGPHOS)-$(\mathrm{AuCl})_2$	8.59 × 10^{29}	1188
k	(R)-(DTBM-SEGPHOS)-$(\mathrm{AuBr})_2$	7.41 × 10^{29}	1733
l	(R)-(TolBINAP)-$(\mathrm{AuCl})_2$	8.52 × 10^{29}	1145
m	(R)-(DTBM-SEGPHOS)-$(\mathrm{AuCl})_2$	7.06 × 10^{29}	1644

[a] For each compound, the molecular density (MD) and the molecular weight (MW) are given. [b] See the SI for the structures of the complexes.

Table 2. Values of the Fixed Diffusion Coefficients for the Two Compounds Used as Internal References

internal reference	log $D_{\mathrm{ref,fix}}$
adamantane in $\mathrm{CD_2Cl_2}$	−8.82
$\mathrm{CH_2Cl_2}$ in $\mathrm{CD_2Cl_2}$	−8.63

Figure 1 shows the normalized diffusion coefficients for a set of 13 gold complexes, plotted against the known molecular weight of each compound. Molecular weights actually range from 350 to 1733 g/mol, and molecular densities range from 6.63 × 10^{29} to 12.8 × 10^{29} g/(mol·m^3).

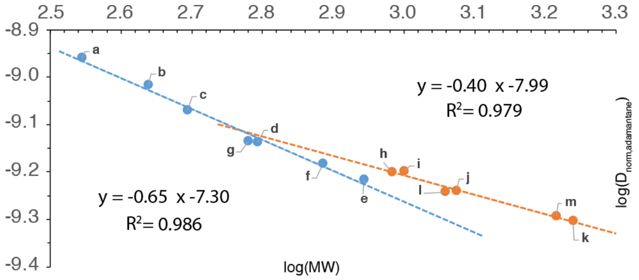

Figure 1. log D versus log MW in $\mathrm{CD_2Cl_2}$. All compounds were normalized to log $D_{\mathrm{ref,fix}}$ (adamantane).

A qualitative analysis revealed that the data in Figure 1 may not be described accurately with a single linear relationship. However, when a separation was made between mono- and digold complexes, a linear relationship was obtained within each group. The parameters for these relationships are summarized in Table 3. Importantly, they may be used to obtain estimates of molecular weights from measured diffusion coefficients, with no need for an additional sample-specific calibration procedure.

Table 3. Parameters for the External Calibration Curves Derived from Diffusion Coefficients of Gold Complexes in CD_2Cl_2

	$-\log K$	$-a$	R^2
monometallic gold complexes	7.30	0.65	0.986
bimetallic gold complexes	7.99	0.40	0.979

The difference in parameters for the calibration curves of mono- and digold complexes may have two different origins. A comparison of the molecular densities of the mono- and digold species shows that the difference in calibration does not arise from it; the average molecular densities for the two groups of complexes differ by less than 3%. On the other hand, the mono- and digold complexes have a different overall shape. Qualitatively, monometallic complexes are mostly spherical-like molecules, while digold complexes have a more elongated shape. This can be appreciated in the three-dimensional structure of the compound, as shown in the SI.

The validity of the proposed external calibration curves has then been checked using the estimate of the molecular weights of compounds that were left out of the data set for the linear regressions shown in Figure 1. Table 4 shows the estimated molecular weights for $(Ph_3P)AuMe$ as a monometallic complex and R-(BINAP)-$(AuCl)_2$ as a bimetallic complex, as obtained from the diffusion measurements shown in Figure 2, with adamantane as an internal reference. For both compounds, the estimated molecular weight differs from the known value by 3.7 and 0.4% when using the calibration curve derived from the corresponding number of gold atoms. In contrast, using the calibration curve derived for low-density compounds (classical ECC), errors of 25 to 45% were observed, depending on the predicted shape (Table 4). Conversely, large errors were also observed when the ECC derived for monogold species was used for the digold species.

Table 4. Comparison between the Calculated and the Estimated Molecular Weights for Two Gold Complexes Using Adamantane as a Reference and the ECCs of ref 39 (classic-ECC) or the ECCs Introduced Here for Mono- (G1) or Digold (G2) Complexes

		MW_{est} (g/mol)				
		classic-ECC			gold-ECC	
	MW (g/mol)	merged[a]	DSE[b]	ED[c]	G1	G2
(BINAP)-$(AuCl)_2$	1087	751	664	561	864	1083
$(Ph_3P)AuMe$	474	377	351	347	492	437

[a] Merged calibration curves can be used if the molecular shape is unknown. [b] Dissipated spheres and ellipsoids. [c] Expanded discs.

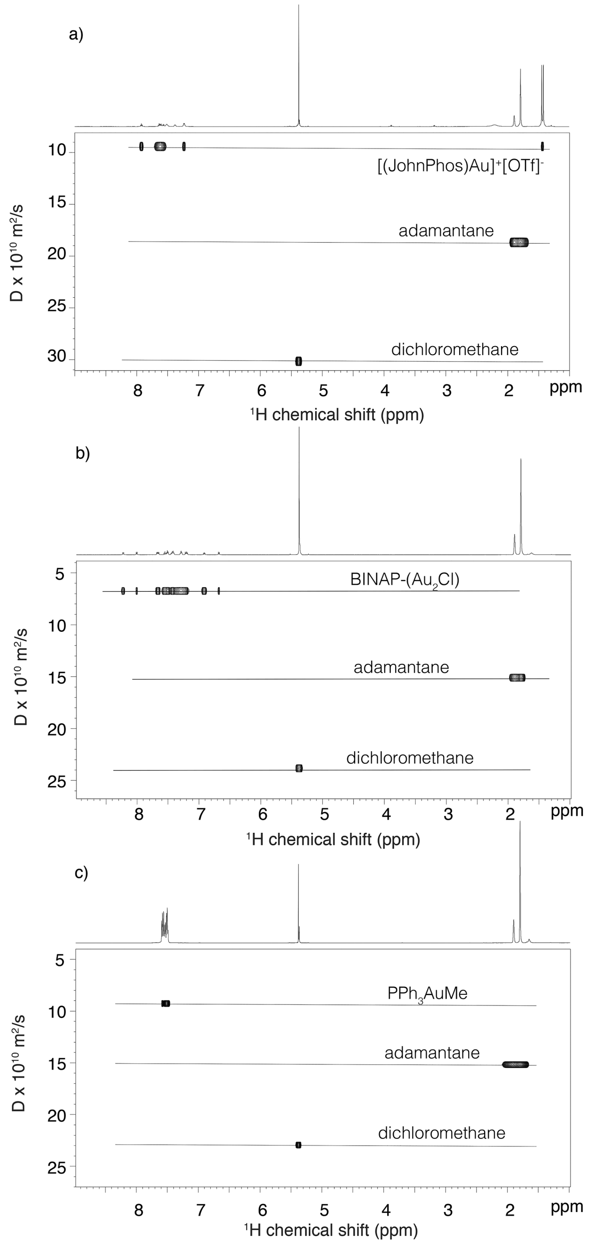

Figure 2. ^1H DOSY NMR of (a) [(JohnPhos)Au] + [OTf]-, (b) (BINAP)-$(AuCl)_2$, and (c) $(Ph_3P)AuMe$ complexes in CD_2Cl_2 with internal references (adamantane).

One of the proposed advantages of the ECC approach is the possibility to use a variety of internal references, with no need to recalculate the calibration curve. Table 5 shows the estimated molecular weights for the compounds analyzed

Table 5. Comparison between the Calculated and the Estimated Molecular Weights for Two Gold Complexes Using CD_2Cl_2/CH_2Cl_2 as a Reference and the ECCs of Ref 39 (classic-ECC) or the ECCs Introduced Here for Mono- (G1) or Digold (G2) Complexes

		MW_{est} (g/mol)				
		classic-ECC			gold-ECC	
	MW (g/mol)	merged	DSE	ED	G1	G2
(BINAP)-$(AuCl)_2$	1087	760	672	566	858	1037
$(Ph_3P)AuMe$	474	359	335	335	477	430

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Table 6. Comparison between the Calculated and the Estimated Molecular Weights for Three Gold Complexes[a]

mixture	expected compound	calculated MW (g/mol)	estimated MW (g/mol) gold-ECC G1	 G2	$\Delta_{\%}$
(JohnPhos)AuCl		531	561		5.3
(JohnPhos)AuCl + AgOTf	$[(\text{JohnPhos})\text{Au}]^+[\text{OTf}]^-$	644	611		5.4
(JohnPhos)AuCl + AgOTf + 1-pentyn-1-ylbenzene	$[(\text{JohnPhos})\text{Au}(\text{H}_7\text{C}_3\text{C}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	788	770		2.3
(JohnPhos)AuCl + AgOTf + phenylacetylene	$[(\text{JohnPhos})\text{Au}(\text{HC}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	746	786		5.1
(IPr)AuCl		622	638		2.5
(IPr)AuCl + AgOTf	$[(\text{IPr})\text{Au}]^+[\text{OTf}]^-$	736	699		5
(IPr)AuCl + AgOTf + 1-pentyn-1-ylbenzene	$[(\text{IPr})\text{Au}\ (\text{H}_7\text{C}_3\text{C}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	880	833		5.3
(IPr)AuCl + AgOTf + phenylacetylene	$[(\text{IPr})\text{Au}\ (\text{HC}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+,\text{OTf}^-$	838	1033		23
	$[\{(\text{IPr})\text{Au}\}_2(\eta^1,\eta^2\text{-C}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	1424		1444	1.4
(Ph_3P)AuCl		494	501		1.4
(Ph_3P)AuCl + AgOTf	$[(\text{Ph}_3\text{P})\text{Au}]^+[\text{OTf}]^-$	610	621		1.8
(Ph_3P)AuCl + AgOTf + 1-pentyn-1-ylbenzene	$[(\text{Ph}_3\text{P})\text{Au}(\text{H}_7\text{C}_3\text{C}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	754	743		1.5
(Ph_3P)AuCl + AgOTf + phenylacetylene	$[(\text{Ph}_3\text{P})\text{Au}(\text{HC}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$	718	737		2.6

[a]The estimated molecular weights were obtained from a normalized diffusion coefficient measured in CD_2Cl_2 using adamantane as an internal reference and the gold-ECCs for mono- or digold complexes.

above, now using the measured diffusion coefficient of the solvent as a reference. Strikingly, the results are comparable to those obtained using adamantane, with errors of 0.6 and 4.8% for the estimated molecular weights.

One of the main potential applications of our ECCs is in the analysis of molecular interactions in gold-catalyzed reactions. The estimated molecular weight of a chemical species gives information on its association with other compounds. This is illustrated here with a cationic gold complex, obtained in situ by reacting (JohnPhos)AuCl with AgOTf in CD_2Cl_2 and filtering the AgCl precipitate. Using the ECC derived with monogold species and adamantane as an internal reference, the estimated molecular weight is 611 g/mol, as shown in Table 6. Compared to the actual molecular weight of $[(\text{JohnPhos})\text{Au}]^+$, 495 g/mol, and that of the ion pair formed with the $[(\text{JohnPhosAu})]^+[\text{OTf}]^-$ counterion, 644 g/mol, the best agreement clearly is with the ion pair. This is a firm indication of a strong association in solution. This observation can be validated by performing a ^{19}F PFG NMR experiment. Figure 3 shows that the measured diffusion coefficient obtained from the $[\text{OTf}]^-$ ion ^{19}F nuclei is close to that obtained for the JohnPhos ^{1}H signals. This example illustrates the usefulness of external calibration curves, with which the type of pairing can be characterized by observing just one of the partners. Similar results and information were obtained with two other examples, with a phosphine and an NHC (N-heterocyclic carbene) ligand, as shown in Table 6 (mixtures in rows six and ten).

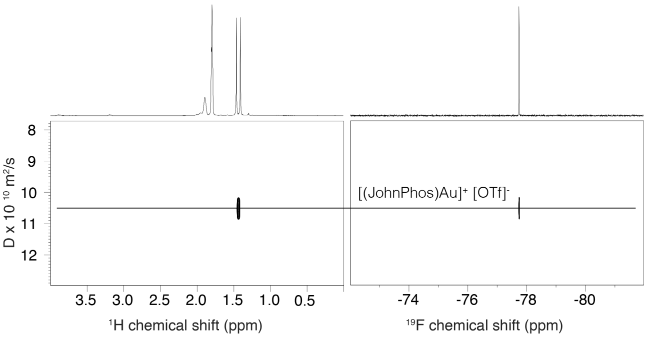


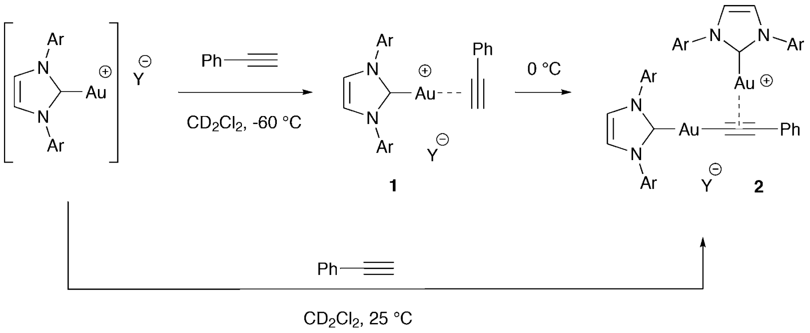
Figure 3. ^{19}F and ^{1}H DOSY for the $[(\text{JohnPhos})\text{Au}]^+[\text{OTf}]^-$ catalyst in CD_2Cl_2.

A further step can be taken with the analysis of mixtures containing a cationic gold complex and an excess of alkyne, which would be representative of the numerous gold-catalyzed alkyne transformations reported in the literature.[41−43] Table 6 also shows the diffusion coefficients measured from the ligand ^{1}H signals of gold complexes after the addition of an alkyne for three complexes and two alkynes. In five cases, the estimated molecular weights obtained with the G1-ECC curve reveal that the cationic gold complex strongly associates with the alkyne, with a deviation of less than 6% between the estimated and the calculated molecular weight of the adducts. This corresponds to the expected formation of gold π-alkyne complexes,[44−46] which is central to a number of important gold-catalyzed reactions. This process, however, also depends on alkyne substitution and on the nature and structure of the ligand.

Interestingly, the diffusion coefficient and estimated molecular weight obtained for the mixture of complex $[(\text{IPr})\text{Au}]^+[\text{OTf}]^-$ and phenylacetylene with G1-ECC is 1033 g/mol, which does not correspond to a simple gold π-alkyne complex with formula $[(\text{IPr})\text{Au}(\text{HC}{\equiv}\text{C}-\text{C}_6\text{H}_5)]^+[\text{OTf}]^-$, which has a molecular weight of 796 g/mol. This is, however, fully consistent with the observation made by Widenhoeffer et al. Indeed, when $[(\text{IPr})\text{Au}]^+[\text{OTf}]^-$ and phenylacetylene were reacted in CD_2Cl_2 at 25 °C, the formation of a gold acetylide was observed, in which the alkyne moiety still serves as a π ligand for a second gold ion, as in $[((\text{IPr})\text{Au})_2\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{C}-\text{C}_6\text{H}_5]^+[\text{OTf}]^-$ (Scheme 1, **2**), as evidenced by the disappearance of the acetylenic proton at $\delta = 4.56$ ppm in the ^{1}H NMR spectrum as well as by X-ray characterization.[44] Using G2-ECC, an estimated molecular weight of 1444 g/mol was obtained, which is consistent with the calculated molecular weight of 1424 g/mol for **2**. This example clearly illustrates the usefulness of the ECC for analyzing the structure of gold π-alkyne complexes.

The use of empirical relationships between diffusion coefficients as measured by PFG NMR becomes more complicated when multiple species coexist and interconvert.[47]

Scheme 1. Ar = 2,6-Diisopropylphenyl and Y = OTf or SbF_6[a]



[a] See ref 15a.

When chemical exchange is fast on the NMR and diffusion-encoding time scales, the apparent diffusion coefficient will be a compromise that depends on the diffusion coefficients and exchange rates of the interconverting species. As a result, an unexpected value of the estimated molecular weight for an organometallic species may also be an indication that chemical exchange is present.[48] The effects of dynamics on apparent diffusion coefficients can be limited by working at low temperature, as was done in analyses of organolithium compounds.[49,50]

The proposed method was also assessed for concentrations of the compounds that are closer to those found in catalytic reactions. As shown in the Supporting Information, comparable estimates of molecular weights are obtained at a concentration 10 times smaller than for the cationic gold complexes analyzed here along with their reaction with an alkyne substrate. Overall, the ECC approach proves very useful from an experimental point of view because it can provide accurate results without the need to add potentially reactive compounds to the solution.

CONCLUSIONS

We have shown that pulsed-field gradient (PFG) NMR together with external calibration curves can be used to obtain information on the interaction of gold(I) complexes with their counterion and substrates. While the original calibration curves derived for compounds with low molecular density are not applicable to gold complexes, a new set of parameters provide estimates of molecular weight with much-improved accuracy. This is illustrated with several cationic gold complexes, counterions, and complexation with alkynes. The proposed approach is straightforward and has the potential to aid in the understanding of the mechanism of gold-catalyzed reactions.

METHODS

The external calibration curve (ECC) approach is briefly described here. For a more detailed explanation, see ref 36. Diffusion coefficients obtained from pulsed-field gradient (PFG) NMR experiments are highly sensitive to experimental conditions and parameters. In order to attenuate the influence of sources of systematic errors (e.g., gradient calibration, temperature effects...), the diffusion coefficient measured for the compound of interest D_x is divided by that of a reference compound D_{ref} present in the solution. Then, the resulting relative diffusion coefficient is multiplied by a so-called fixed value of the diffusion coefficient of the reference compound $D_{\text{ref,fix}}$ so that the same calibration curve can be used irrespective of the choice of the reference compound. This fixed value is obtained by means of a series of measurements carried out on the reference compound under identical experimental conditions. These quantities are usually manipulated in log form, and the resulting definition of the normalized diffusion coefficient $D_{x,\text{norm}}$ is

$$\log(D_{x,\text{norm}}) = \log(D_x) - \log(D_{\text{ref}}) + \log(D_{\text{ref,fix}}) \tag{1}$$

The calibration curve approach then relies on the empirical assumption that a power law relates the normalized diffusion coefficient to the molecular weight of the analyte:

$$\log(D_{x,\text{norm}}) = \log(k) + \alpha \log(\text{MW}) \tag{2}$$

Parameters k and α are obtained from a linear regression between $\log(D_{x,\text{norm}})$ and the known molecular weight for a series of compounds. Once ECC parameters k and α are determined, the molecular weight of an unknown compound can be estimated with the relationship

$$\text{MW}_{\text{estimated}} = 10^{(\log(D_{x,\text{norm}})-\log(k)/\alpha)} \tag{3}$$

EXPERIMENTAL SECTION

Sample Preparation for Neutral Gold Complexes LAuX or L-$(AuX)_2$ (X = Cl, Br, OH). For each gold complex, a solution was prepared in 600 μL of CD_2Cl_2 at a concentration of 33 mM. In each solution, adamantane was added at a concentration of 33 mM (2.7 mg) to be used as a reference. Undeuterated dichloromethane (CH_2Cl_2) was also added, at a concentration of 33 mM (1.7 mg), for a separate application. In the following sections, the resonances of CH_2Cl_2 and $CDHCl_2$ were integrated simultaneously.

Sample Preparation for Cationic Gold Complexes $[LAu]^+[OTf]^-$. The gold chloride precursor ((JohnPhos)AuCl, 10.6 mg; (IPr)AuCl, 12.4 mg; or (Ph_3P)AuCl), 9.9 mg) was weighed into a glass vial. CD_2Cl_2 (600 μL) was then added using a syringe. Silver triflate (5.14 mg, 1 equiv) was added, and the vial was sonicated for 3 min at room temperature. The content of the vial was filtered over Celite, and the clear solution was transferred into the NMR tube previously charged with adamantane (5 mg). Undeuterated dichloromethane (CH_2Cl_2) was also added (3 μL) in the case of $[(\text{JohnPhos})\text{Au}]^+[\text{OTf}]^-$.

NMR Experiments. All of the experiments were performed on a 600 MHz Bruker Avance spectrometer using a 5 mm TXI probe with actively shielded triple-axis gradients at a nominal temperature of 298 K. Sample spinning was deactivated. All of the DOSY experiments were performed using a double stimulated echo sequence with bipolar gradient pulses with convection compensation. The diffusion time ranged from 150 to 230 ms. The delay for gradient recovery was 0.2 ms, and the eddy current delay was 5 ms. For each DOSY-NMR experiment, a series of 8 spectra of 32 768 data points were collected over a total experiment time of 22 min. The gradient amplitude was increased in increments from 6.5 to 45.5 G cm^{-1} for the maximum gradient strength in a linear ramp. Diffusion coefficients were calculated by a monoexponential fit with the T1/T2 analysis module of the topspin software or the Dynamics Center software (Bruker, Billerica, U.S.A.).

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The diffusion coefficients of 13 gold complexes were measured in deuterated dichloromethane solvent, and adamantane was used as an internal reference to establish the calibration curves. Undeuterated dichloromethane was also employed to test the possibility to use another internal reference, using ECCs calculated with adamantane. The fixed diffusion coefficients of adamantane and dichloromethane ($D_{\mathrm{ref,\ fix}}$) were determined by averaging the values obtained in 13 separate experiments.

Molecular Geometry. The geometries of the gold complexes (**a**, **b**, **c**, **d**, **e**, **g**, **i**, and **l**) were obtained from the CCDC X-ray structure database when available. All other structures for complexes **f**, **h**, **j**, **k**, and **m** were optimized using the Gaussian 09 software package at the B3LYP level of density functional theory (DFT). The gold and the bromine atoms were described by the LANL2DZ ECP basis set. All other atoms were described by the 6-31G(d,p) basis set. (See the SI for details.)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00709.

> Calculation of the molecular van der Waals density MDW, 3D geometries and chemical structures of the model compounds used for ECCs, influence of concentration, ^{1}H 1D NMR spectra of compounds LAuX, and abbreviations (PDF)
>
> Coordinates of the computed structures (XYZ)

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Notes

The authors declare no competing financial interest.

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