

Selectively Measuring p Back-Donation in Gold(I) Complexes by NMR Spectroscopy

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Abstract: Even though the Dewar–Chatt–Duncanson model has been successfully used by chemists since the 1950s, no experimental methodology is yet known to unambiguously estimate the constituents (donation and back-donation) of a metal–ligand interaction. It is demonstrated here that one of these components, the metal-to-ligand p back-donation, can be effectively probed by NMR measurements aimed at determining the rotational barrier of a C–N bond (D_{Hr}) of a nitrogen acyclic carbene ligand. A large series of gold(I) complexes have been synthesized and analyzed, and it was found that the above experimental observables show an accurate correlation with back-donation, as defined theoretically by the appropriate charge displacement originated upon bond formation. The proposed method is potentially of wide applicability for analyzing the ligand effect in metal catalysts and guiding their design.

Introduction

The Dewar–Chatt–Duncanson (DCD)^[1,2] model has been high in chemists' favor.^[3] It gives a simple picture of the bond between an unsaturated substrate and a transition metal in terms of s donation and p back-donation. Despite its popularity, the evaluation of the relative contribution of its two components remains a challenge. Indeed, available experimental techniques, including the popular Tolman^[4] and Lever^[5,6] electronic parameters, do provide an estimate of the net donor power of a ligand, but cannot disentangle the DCD components. More recent efforts aimed at extracting the electronic properties of N-heterocyclic carbene (NHC) ligands from experimental observables^[7–10] are very relevant here, but if and how an experimental observable depends on the DCD bonding components remains very difficult to ascertain.^[10,11]

Recently, building upon an unambiguous definition of the donation and back-donation charges based on the charge displacement function (CDF),^[12] some of the present authors have demonstrated that the DCD components can be disentangled and effectively extracted by looking at simple experimental observables.^[13] It was then argued that the approach can in principle be used to identify experimental observables that selectively depend on a specific DCD component, and we build here on that principle.

The seminal work, more than 50 years ago,^[14,15] by Fischer and Maasbøl related qualitatively the rotation of the heteroatom–carbenic carbon bond to the extent of back-donation in Fischer's carbenes (Figure 1 a). On similar grounds, the groups of Fürstner^[16] and Hashmi^[17] have recently synthesized and characterized catalytic intermediates of Au^I bearing s-bonded organic substrates (Figure 1 b and c), with the aim of analyzing the nature of the Au–C bond. These gold–carbenoid intermediates are receiving increasing attention^[18–26] because the gold–carbene versus gold-stabilized carbocation character may be selectively tuned by the proper choice of the ancillary ligand (L)^[27–30] opening the way to a new rational ligand-controlled gold catalysis. The Au–C bonds in Figure 1 b and c can be described with two limit resonance structures: one implying a pure C \rightarrow Au s donation with the formal positive charge located on the heteroatom of the substrate^[31] (cationic structure), the other implying also a complete Au \rightarrow C p back-donation and having the formal positive charge on the metal (carbenic structure). One may expect that the relative importance of these two limit structures is related to the proper rotational

barrier of a C—C bond for S3/S4 or C—N bond for S5/S6 (Figure 1 b and c). A systematic analysis based on this approach appears very promising to reveal the metal—carbon bond order but, to the best of our knowledge, it was applied only to the two systems of Figure 1 b and c.

This prompted us to look for a class of gold—carbene compounds suitable for investigation, and our choice fell on $[\text{LAu}(\text{NAC})]^{+0}$ (NAC = nitrogen acyclic carbene)^[32,33] since:

1) such complexes are stable; 2) being acyclic, they undergo rotation of the C—N bond; 3) they can be easily synthesized; and finally, 4) the complexes present two limit structures, with

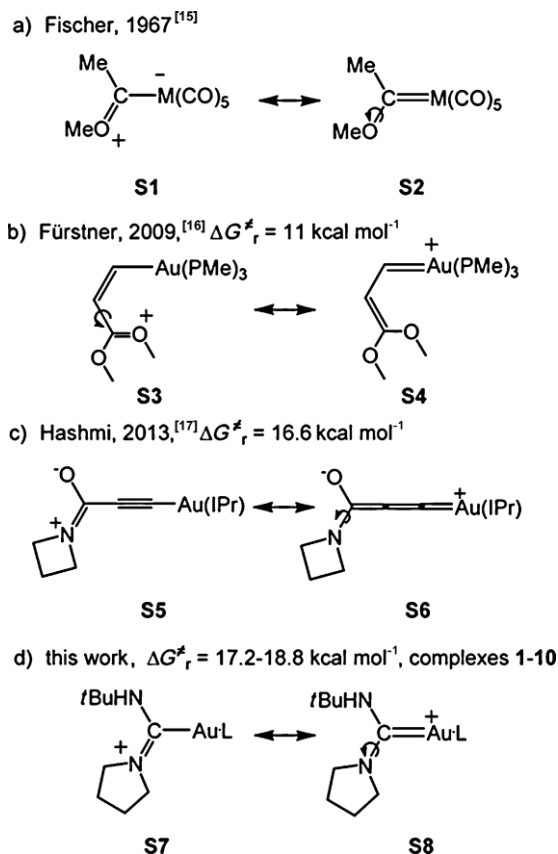


Figure 1. Comparison between: a–c) previous experimental works, and d) this work.

the double bond localized between the gold and the NAC (S8, Figure 1 d) or between the carbon and the nitrogen bearing the pyrrolidine (S7, Figure 1 d).^[34]

In the present work, we report the synthesis of ten $[\text{LAu}(\text{NAC})]^{+0}$ complexes, with L varying among different classes of ligands (complexes 1–10, Figure 2) and the results of a VT-EXSY (variable temperature exchange spectroscopy) NMR^[35] study aimed at evaluating the rotational barrier of the C—N(pyrrolidine) bond (Figure 1 d). We further show, through a detailed theoretical analysis of the CDF describing the formation of the Au^I—carbon bond and its DCD components, that the rotational barrier exhibits a clear correlation with the amount of metal to NAC p back-donation.

Results and Discussion

Synthesis and NMR measurement of rotational barriers

The syntheses for compounds 1–10 presented satisfactory yields with high purity (Figure 2).

For the specific synthetic strategies see the Experimental Section and Supporting Information. Our

selection of the ancillary ligands covers many classes of ligands commonly used in coordination and organometallic chemistry. Some of these ligands give rise to effective catalysts and find a wide range of applications in gold(I) catalysis.^[36] All complexes have been fully characterized by NMR spectroscopy (see the Supporting Information) and are present in solution as a single isomer, since rotation of the NH(*t*Bu) moiety is prevented by the severe steric hindrance between the pyrrolidine and its *tert*-

butyl group.^[37] Moreover, the 180° rotation of the pyrrolidine moiety around the C—N bond, accessible at room temperature,

does not alter the molecule at all. Since all the complexes bear an acidic NH moiety, which is in principle able to strongly interact with the anion in apolar solvents,^[38] we chose to carry out our study in deuterated methanol, in order to minimize any ion-pairing phenomenon and, consequently, any anion influence on DH_r .¹⁶ The rotation rate constant (k_r) of the pyrrolidine, which is related to the C—N bond order,^[39] was obtained using the VT-¹H-EXSY NMR technique, which already proved to be effective in the measurement of activation parameters.^[40–42] The measurement of k_r is based on the exchange of the non-equivalent protons A and B of the pyrrolidine ring, due to the rotation around the C—N bond. This gives two off-diagonal peaks in the 2D spectra (Figure 3 a and b, example for complex

9), the volume of which is related to the rotation rate (see the Experimental Section and Supporting Information). Measuring k_r at different temperatures, DH_r can be evaluated through a simple Eyring plot (see the Supporting Information).

The activation enthalpy (DH_r) presents a significant ligand effect, going from 17.6 (for 1) to 20.0 kcal mol⁻¹ (for 6; Table 1), while the entropic contribution is small with all the ligands (below 4 cal K⁻¹ mol⁻¹, Table 1), consistent with an intramolecular process. Experimental results

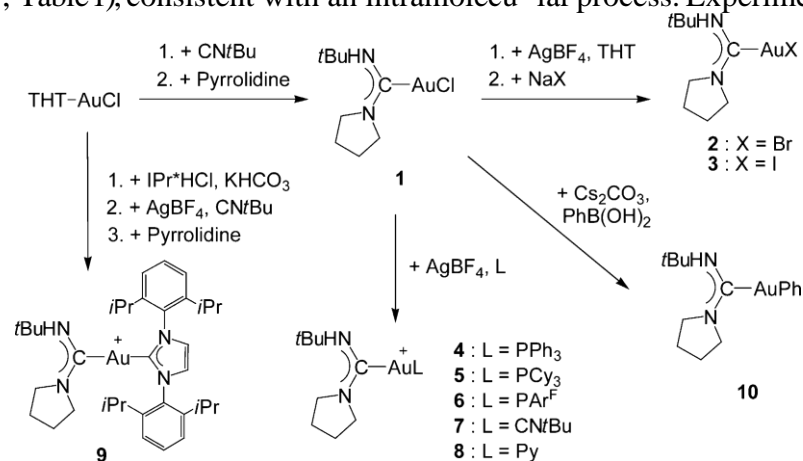


Figure 2. Synthetic routes for complexes 1–10. PAr^F indicates tris-[(3,5-(trifluoromethyl)phenyl)]phosphine, IPr indicates 1,3-bis(2,6-diisopropylphenyl)imidazol-2-yliden).

show an evident differentiation between anionic L (DH_r

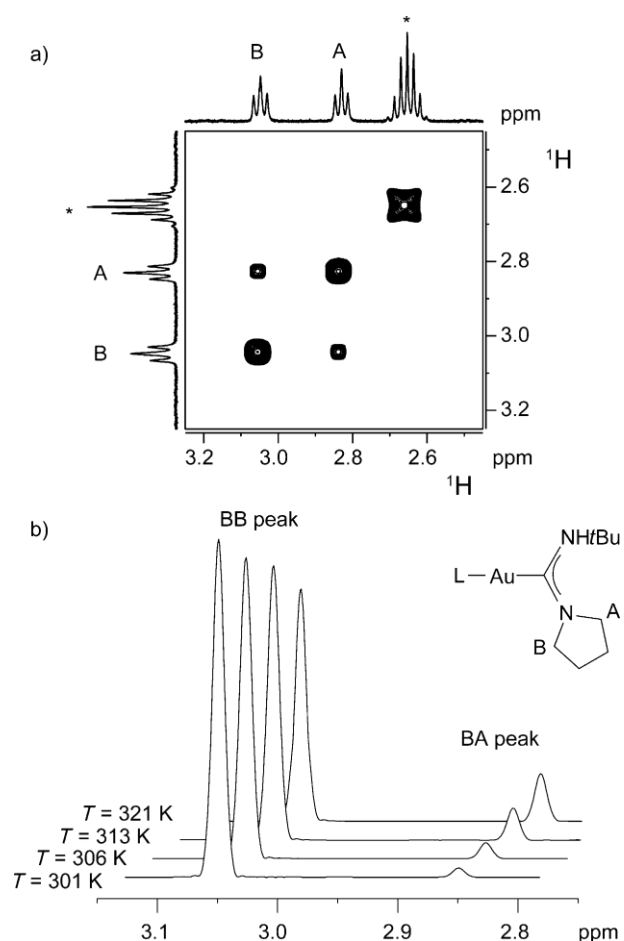


Figure 3. a) VT-¹H-EXSY NMR spectrum of 9 (400.13 MHz, 315 K, CD₃OD, mixing time= 120 ms); * denotes a resonance of the IPr ligand. b) Stacked traces extracted at d_H=3.05 ppm from EXSY NMR spectra recorded at different temperature (mixing time = 0.25 s).

18.5 kcal mol⁻¹) and neutral ones (DH_r^{1/6} > 19.5 kcal mol⁻¹). Such a difference can be explained considering that anionic ligands make the metal more electron-rich, favoring structure S8. Notably, the trend among anionic ligands well correlates with the kinetic trans effect (Cl⁻ < Br⁻ < I⁻ < Ph⁻).^[14]

Table 1. Experimental activation parameters (DH _r ^{1/6} and DS _r ^{1/6}) of the rotation around the C—N bond for [LAu(NAC)] complexes 1–10, along with CT _{tot} , CT _{don} and CT _{back} values (in electrons) for model complexes 1a–10a, [LAu(NAC ^{sym})] ⁺⁰ .					
L	Complex 1–10		Complex 1a–10 a		
	DH _r ^{1/6} [kcal mol ⁻¹]	DS _r ^{1/6} [cal K ⁻¹ mol ⁻¹]	CT _{tot}	CT _{don}	CT _{back}
Cl	17.6 T 0.2	1.2 T 0.6	0.102	—0.108	
Br	17.9 T 0.2	2.3 T 0.8	0.210	—0.105	
I	18.1 T 0.4	2.2 T 1.4	0.114	—0.098	
PPh ₃	19.7 T 0.2	3.6 T 0.6	0.219	—	
PCy ₃			0.132		

PAr ^F	19.6T0.4	3.3T1.2	0.230	-
CNt	20.0T0.4	3.9T1.2	0.247	- -
Bu	19.6T0.2	3.1T0.8	0.220	- -0.045
Py	19.1T0.4	3.8T1.4	0.269	- -0.057
IPr	19.1T0.2	3.2T0.8	0.202	-0.052
Ph	18.3T0.2	1.2T0.8	0.247	-0.092
			0.229	
			0.286	
			0.174	
			0.226	
			0.106	
			0.198	

On the contrary, DH_r does not correlate (correlation coefficient of linear regression, R^2 is 0.753, Figure S14 in the Supporting Information) with the Tolman electronic parameter (TEP)^[4] (an experimental measure of the electron-donor ability of L) of the corresponding ligands.^[43,44] For example, the experimental results reveal that complexes 4 and 5, bearing PPh_3 and PCy_3 as ligands, respectively, have very similar values of DH_r ¹⁶ but the difference in the TEP values is significant (2068 and 2056.4 cm^{-1} , respectively). Similarly, the compound with pyridine (8) presents a DH_r ¹⁶ close to that bearing the NHC (9), but a TEP value considerably higher (by about 21.5 cm^{-1}).^[45] A detailed theoretical analysis of these contrasting considerations appears highly desirable.

Correlation between rotational barrier and back-donation

Our aim here is to provide a quantitative picture of the relation between the nature of the Au—C bond, its bond order and the barrier to rotation, DH_r . It is well known that the analysis of simple structural data, such as the Au—C length, is of little help^[12,28,46] and a more stringent analysis is thus required. We base this on the well-established definition of the donation and back-donation charges provided by the analysis of the symmetry components of the CDF^[13,47,48] (see the Experimental Section and Supporting Information). In order to apply this approach, we need to refer to more symmetric model systems $[LAu(NAC^{sym})]^{+/0}$ (1 a–10 a) in which we substitute the NAC moiety with a simplified symmetric version $(NHMe)_2C$, having two —NHMe moieties bound to the carbenic carbon atom (indicated hereafter as NAC^{sym} , see Figure 4 a and b and the Supporting Information for the structures). In this way, most of the complexes present a symmetry plane passing through the metal center and the N—C—N atoms of NAC^{sym} and this allows us to use C_s symmetry (with A' and A'' irreducible symmetry representations) to separate the DCD components of the CDF.

In all the cases, the fragments used are $[LAu]^{+/0}$ and $[NAC^{sym}]$, with the aim to analyze the charge displacement between the metal fragment and the carbene. It should be stressed that the introduction of NAC^{sym} does not significantly alter the properties of the Au—C bond: both Au—C distances and interaction energies for the two series of complexes, $[LAu(NAC)]^{+/0}$ and $[LAu(NAC^{sym})]^{+/0}$, show a stringent linear correlation (see Figures S15 and S16 in the Supporting Information). Complexes 4 a, 5 a, 6 a, bearing PPh_3 , PCy_3 , and PAr^F , respectively, do not possess the symmetry plane, due to the “helical” orientation of substituents at the phosphorous. In these cases only the net $NAC \rightarrow Au$ charge transfer (CT) can be reported (Table 1). As an example, Figure 4 a–c show the results of our analysis for 1 a, $[ClAu(NAC^{sym})]$ (for details see the Supporting Information). The 3D contour plot of the electron density difference, related to the A symmetry (Figure 4 a), shows a depletion of electron density at the carbenic carbon (gray isosurface) exactly in the region of the donating lone-pair and an accumulation (black isosurface) in the Au—C region toward the gold site (this symmetry correlates with the donation component involving the occupied s orbital of the NAC^{sym} described by the lone pair of the carbenic carbon and the partially empty s orbitals of AuCl).

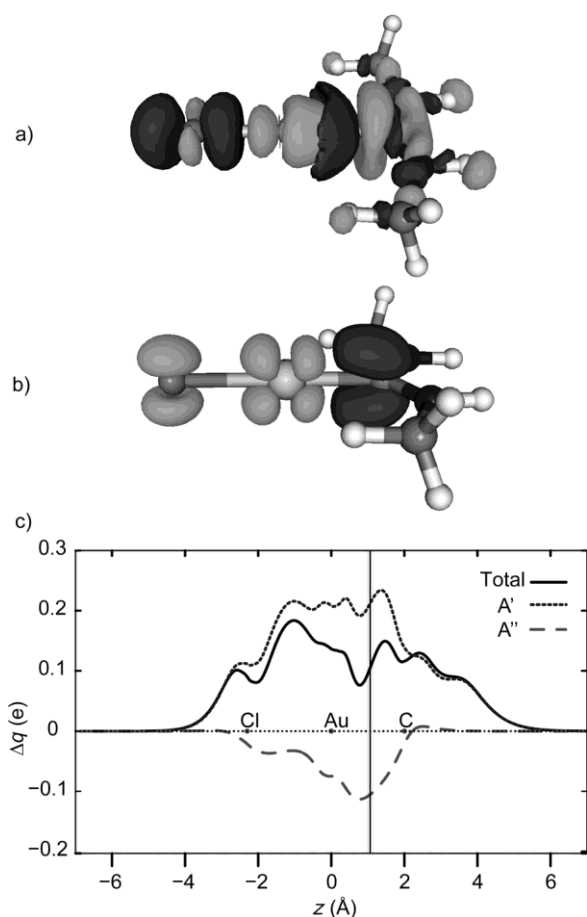


Figure 4. a, b) Three dimensional plots of the electron density difference for: a) A' , and b) A'' symmetry for complex 1a (see main text). Gray isosurfaces identify charge depletion area, black isosurfaces charge accumulation. Density value at the isosurface: $T 0.002 \text{ e au}^{-3}$. c) Charge displacement curves for complex 1a. The vertical band shows a suitable boundary between AuCl and NAC^{sym} fragments.

In case of A'' symmetry (Figure 4 b) a clear charge depletion is present only at the site of AuCl accompanied by a corresponding significant accumulation at the carbenic site (back-donation component).

The two symmetry CDFs (Figure 4 c) give the desired quantitative picture of the nature of the Au—C bond. They clearly show two charge fluxes moving in opposite directions across the whole molecular space, in the expected correspondence with their respective symmetries. By fixing a boundary plane to separate the fragments within the complex (see the Experimental Section) one can extract suitable numerical values of CT between the metal fragment and NAC^{sym} . In this case (complex 1 a) the net CT (CT_{tot}) from NAC^{sym} to AuCl is 0.102 electrons, resulting from a donation of 0.210 e and a back-donation of 0.108 e. The results for all complexes (1 a–10 a) are summarized in Table 1 (the corresponding CDFs are reported in the Supporting Information). The range of variation of the DCD components of the bond is significant. The Py and Ph ligands (8a and 10 a) induce the largest and smallest s-acidity to the metal fragment ($[\text{LAu}]^{+/0}$), respectively. The back-donation,

CT_{back} , varies from -0.045 to -0.108 e for complexes 7a (bearing CNtBu) and 1a (Cl^-), respectively.

Our most important question now is whether a demonstrable relationship exists between CT_{back} and $DH_r^{1/6}$, and Figure 5 shows that a reasonable linear correlation indeed exists for all complexes (1a–3a and 7a–10a) with a correlation coefficient of 0.971. Compounds with a smaller C–N rotational barrier show a larger back-donation component of the Au–C bond (larger magnitude of CT_{back}) and vice versa. This finding is nicely confirmed by theoretical calculations. The computed rotational barrier versus CT_{back} reproduce the same linear trend (Figure S17 in the Supporting Information). Note that, by theoretically extending the range of ligands, including for instance the carbonyl complex $[COAu(NAC)]^+$ (where the back-donation ability of the metal fragment is almost vanishing, CT_{back} is just of 0.02 e), the linear correlation is preserved (R^2 is 0.991).^[49] It is important to note that the rotational barrier does not show any correlation with the donation component CT_{don} ($R^2 = 0.397$, see Figure S18 in the Supporting Information) and, therefore, only a poor correlation with the overall net donation ($R^2 = 0.889$, see Figure S19 in the Supporting Information).

It is somewhat unsatisfactory that the three phosphorus ligands in 4a–6a, which induce strong net acidity at the metal fragment, escape the previous analysis. We can, however, adopt a different, indirect approach, which includes all the

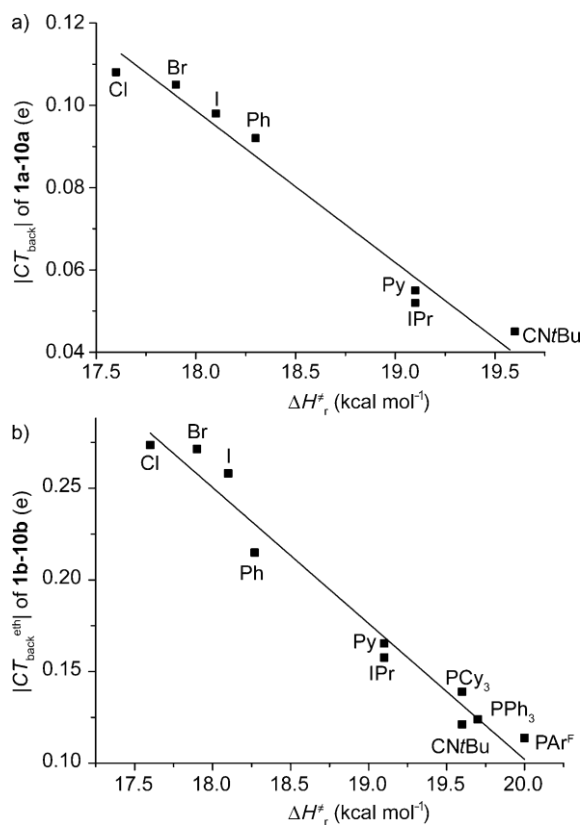


Figure 5. a) Linear correlation ($R^2 = 0.971$) between the C–N rotational barrier ($DH_r^{1/6}$) for complexes 1–10 and the absolute value of the CT_{back} in $[LAu-(NAC^{\text{sym}})]^{+/0}$ (see Table 1). b) Linear correlation ($R^2 = 0.976$) between the C–N rotational barrier (DH_r) for complexes 1–10 and the absolute value of the CT_{ethyl} in $[(L)Au(C_2H_2)]^{+/0}$ model systems (1b–10b).

ligands and, at the same time, provides a powerful, independent, verification and generalization of the correlation between rotational barrier and ability of the metal fragment $[LAu]^{+/0}$ to give back-donation. To do this, we theoretically analyze a different series of complexes, 1b–10b, of structure $[LAu(C_2H_2)]^{+/0}$, where the ligands L are the same as in the corresponding 1a–10a series, while ethyne replaces the NAC. We have previously demonstrated^[13] that the distortion of ethyne from linearity upon coordination to a metal center depends very precisely [see Eqs. (4) and (5) in the Experimental Section] on the metal (C₂H₂) p back-donation (CT_{ethyl}), with a small contribution of the (C₂H₂)M s donation (CT_{ethyl}), and an even smaller contribution of an electrostatic term. We have computed ethyne distortion and total CT, and

from these, we have extracted the two DCD components of the gold—ethyne bond for the entire L series (1b–10b; Table S2 in the Supporting Information). As Figure 5 b shows, the correlation between the p back-donation ($CT_{\text{back}}^{\text{eth}}$) and the experimental $DH_r^{1/6}$ of complexes 1–10 is indeed very good and the data for ligands 4–6 fit the model nicely. The implications of this finding are remarkable. It clearly suggests that the ligand effect on the p basicity of the metal fragment $[LAu]^{+/0}$ is very similar across different substrates (ethyne or NAC), even having very different p-accepting properties (the magnitude of back-donation to ethyne almost doubles compared to NAC; see Figure 5 a and b). There are a number of other interesting observations that are worth pointing out. We can see again, for example, that complexes bearing Py and IPr have very different CT^{eth} but similar CT_{back} values (and so similar DH_r). The fluorinated phosphine PArF induces the smallest back-donation to the trans ligand, in accord with its highest DH_r . Comparison of PPh₃ and PCy₃ leads to the firm conclusion that the fragment $[(PR_3)Au]^+$, has the same back-donation-inducing ability with either an alkyl or aliphatic substituent R.

This last result is somewhat surprising, considering the different net donor ability of PPh₃ and PCy₃ and the net acidity of the corresponding fragments (CT_{tot} is 0.128 and 0.144 electrons, respectively), and indicates that the gold atom “mediates” the electronic interplay between the two ligands, making intuitive predictions on the ability of a ligand to stabilize the carbenic structure not obvious. Consistently with our results, recent experimental data do indeed indicate that aromatic and alkyl phosphines behave similarly when employed for tuning the carbocation versus carbenoid character of catalytic intermediates of Au I.[16,28,29,50]

CONCLUSION

In summary, we have discovered that an experimental observable determined by NMR techniques—the proper rotational barrier of the CN bond of a NAC ligand bound to a metal (gold in our case)—provides a selective measurement of one DCD bonding component, the metal-to-substrate p back-donation.

This opens the possibility to characterize the electronic structure of the gold metal fragment by actually measuring how its p basicity is affected by the nature of the coordinated ligands. We hope that this method shall contribute to a more rational control of ligand electronic effects in the design of new catalysts. Furthermore, in view of the recent advances in the synthesis of different metal complexes of acyclic carbenes,^[51] one can easily envisage the extension of the method to other metal systems.

Experimental Section

Synthesis

$[ClAu(NAC)]$ (complex 1) is a convenient precursor for the synthesis of other complexes, since the chlorine atom can be easily substituted with a wide variety of other monohapto ligands L, generally by chloride abstraction with a silver salt in the presence of L (see the Supporting Information). For specific target complexes the synthetic route may be different and involve more steps. For example, the synthesis of complex 9 could be achieved, in principle, starting from complex 1, but a different route that starts from the complex $[ClAu(IPr)]$ as intermediate,^[51,52] and then “builds up” the NAC moiety directly on the metal is an even easier, suitable route for the synthesis. For complex 10, the substitution of the chloride with a phenyl is possible by the reaction with a suitable boronic acid, as $PhB(OH)_2$, in the presence of Cs_2CO_3 as a base.^[53]

EXSY NMR measurements

In the EXSY NMR spectrum, the integration of diagonal (AA and BB) and off-diagonal (AB and BA) peaks allows the rotation rate (k_r) to be obtained through Equation (1):

$$k_r = \frac{1}{t_m} \times \ln\left(\frac{r+1}{r-1}\right)$$

where t_m is the mixing time, and:

$$r = \frac{(AA + BB)}{(AB + BA)}$$

Theory and bonding analysis

All calculations were carried out with the density functional theory (DFT). All details are reported in the Supporting Information. The AuC bond was analyzed using the charge-displacement function:[12]

$$\Delta q(z) = \int_{-\infty}^z dz' \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Delta \rho(x, y, z') dx dy$$

where $D1$ is the difference between the electronic density of a complex and that of its non-interacting fragments [LAu] metal substrate and NAC, and z is any suitable axis joining them. Here, we consider the axis joining the gold nuclei position and carbenic carbon of NAC moiety. The CDF gives the exact definition of the amount of electronic charge which, upon formation of the complex, is displaced from left to the right (the direction of decreasing z) across the plane perpendicular to the axis at point z . As previously shown by some of us, for suitable symmetric complexes and fragments, $D1$, and consequently $Dq(z)$, can be decomposed into additive symmetry components which can be readily identified

with the DCD components of the bond.^[47,48,13] All symmetry constrained structures of different complexes are reported in the Supporting Information. In all the cases, the fragments used are [LAu]⁺⁰ and [NAC^{sym}], with the aim to analyze the charge displacement between the metal fragment and the carbene. The curve for the A'' symmetry (dashed line in Figure 4 c) is negative everywhere and shows a continuous flux of electrons from the metal moiety towards the NAC^{sym} fragment (AuNAC^{sym} p back-donation). Consistently, this symmetry correlates with the formally empty out-of-plane p-orbital at the carbenic C. By contrast, the curve of A' symmetry, which correlates with filled in-plane donating lone-pair, is always positive, describing a flux of electrons that goes from the NAC^{sym} towards the metal fragment (NAC^{sym} \rightarrow Au donation). In order to have a reasonable measure of the CT, one has to fix a plausible boundary to separate the fragments within the complex. Our choice is the z point where equal-valued isodensity surfaces of the isolated fragments become tangent. The vertical band in Figure 4 c is centered at that point and has a width equal to 10 % of the bond length, in order to visualize a reasonable uncertainty. The same analysis was carried out for all other systems (see the Supporting Information). The analysis of DCD components in complexes 1 b–10 b was carried out on the basis of the method described in ref. [13], where we demonstrated that the distortion Dq of ethyne from linearity upon its coordination to a metal center depends on the metal(C₂H₂) p back-donation (CT^{eth}), with only a small contribution of the (C₂H₂)M s donation (CT^{eth}), and an even smaller influence of an electrostatic term (Dq_{elect}).

$$\Delta \theta = 7.9|CT_{\text{don}}^{\text{eth}}| + 57.5|CT_{\text{back}}^{\text{eth}}| + \Delta \theta_{\text{elect}} \quad (4)$$

$$CT_{\text{tot}}^{\text{eth}} = CT_{\text{don}}^{\text{eth}} + CT_{\text{back}}^{\text{eth}} \quad (5)$$

By evaluating the total CT between ethyne and the metal fragment (CT^{eth}), Dq and Dq_{elect} , we can evaluate the DCD components, and in particular the Au (C₂H₂) p back-donation (CT^{eth}) through Equations (4) and (5).^[13]

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REFERENCES

- [1] J. S. Dewar, *Bull. Soc. Chim. Fr.* 1951, 18, C71–C79.
- [2] J. Chatt, L. A. Duncanson, *J. Chem. Soc.* 1953, 2939–2942.
- [3] *Modern Coordination Chemistry: The Legacy of Joseph Chatt* (Eds.: N. Winterton, G. J. Leigh), RSC, London, 2002.
- [4] C. A. Tolman, *Chem. Rev.* 1977, 77, 313–348.
- [5] A. B. P. Lever, *Inorg. Chem.* 1990, 29, 1271–1285.
- [6] A. B. P. Lever, *Inorg. Chem.* 1991, 30, 1980–1985.
- [7] M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* 2006, 128, 16514–16515.
- [8] D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* 2007, 26, 6042–6049.
- [9] D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem.* 2008, 120, 2299–2302; *Angew. Chem. Int. Ed.* 2008, 47, 2267–2270.
- [10] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* 2013, 125, 3011–3015; *Angew. Chem. Int. Ed.* 2013, 52, 2939–2943.
- [11] L. Triguero, A. Fçhlisch, P. Väterlein, J. Hasselstrøm, M. Weinelt, L. G. M. Pettersson, Y. Luo, H. Agren, A. J. Nilsson, *J. Am. Chem. Soc.* 2000, 122, 12310–12316.
- [12] L. Belpassi, I. Infante, F. Tarantelli, L. Visscher, *J. Am. Chem. Soc.* 2008, 130, 1048–1060.
- [13] L. Bistoni, F. Tarantelli, L. Belpassi, *Angew. Chem.* 2013, 125, 11813–11816; *Angew. Chem. Int. Ed.* 2013, 52, 11599–11602.
- [14] R. H. Crabtree, in *The Organometallic Chemistry of the Transition Metals*, 4th ed., Wiley, Hoboken, 2005.
- [15] E. O. Fischer, A. Maasbçl, *Chem. Ber.* 1967, 100, 2445–2456.
- [16] G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.* 2009, 121, 2548–2551; *Angew. Chem. Int. Ed.* 2009, 48, 2510–2513.
- [17] M. M. Hansmann, F. Rominger, A. S. K. Hashmi, *Chem. Sci.* 2013, 4, 1552–1559.
- [18] A. S. K. Hashmi, *Angew. Chem.* 2008, 120, 6856–6858; *Angew. Chem. Int. Ed.* 2008, 47, 6754–6756.
- [19] A. M. Echavarren, *Nat. Chem.* 2009, 1, 431–433.
- [20] R. E. Brooner, R. A. Widenhoefer, *Angew. Chem.* 2013, 125, 11930–11941; *Angew. Chem. Int. Ed.* 2013, 52, 11714–11724.
- [21] G. Seidel, B. Gabor, R. Goddard, B. Heggen, W. Thiel, A. Fürstner, *Angew. Chem.* 2014, 126, 898–901; *Angew. Chem. Int. Ed.* 2014, 53, 879–882.
- [22] G. Seidel, A. Fürstner, *Angew. Chem.* 2014, 126, 4907–4911; *Angew. Chem. Int. Ed.* 2014, 53, 4807–4811.
- [23] R. E. Brooner, R. A. Widenhoefer, *Chem. Commun.* 2014, 50, 2420–2423.
- [24] R. J. Harris, R. A. Widenhoefer, *Angew. Chem.* 2014, 126, 9523–9525; *Angew. Chem. Int. Ed.* 2014, 53, 9369–9371.
- [25] M. Joost, L. Esteves, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bour-
issou, *Angew. Chem. Int. Ed.* 2014; DOI: 10.1002/ange.201407684.
- [26] A. Fürstner, *Angew. Chem.* 2014, 126, 8–9; *Angew. Chem. Int. Ed.* 2014, 53, 8–9.
- [27] C. Ferrer, C. H. M. Amijs, A. M. Echavarren, *Chem. Eur. J.* 2007, 13, 1358–1373.
- [28] D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Dq ¼ 7:9jCTdonjþ 57:5jCTbackjþ Dqelect Toste, *Nat. Chem.* 2009, 1, 482–486.
- [29] M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem.* 2010, 122, 2596–2597; *Angew. Chem. Int. Ed.* 2010, 49, 2542.
- [30] Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan, X. Shi, *Angew. Chem.* 2014, 126, 9975–9979; *Angew. Chem. Int. Ed.* 2014, 53, 9817–9821.
- [31] The X-ray crystal structure of the related complex [(Ph)(NMe₂)C]AuCl shows that the C—N distance is 1.262 Å, which is particularly short and essentially double bond. This is an indication that in such a

- case the resonance structure with the formal charge on the nitrogen is particularly stable. Please, see: U. Schubert, K. Ackermann, R. Aumann, *Cryst. Struct. Comm.* 1982, 11, 591 – 594.
- [32] A. S. K. Hashmi, T. Hengst, C. Lothschültz, F. Rominger, *Adv. Synth. Catal.* 2010, 352, 1315 – 1337.
- [33] NACs are also known as acyclic diaminocarbene (ADCs), please see: L. M. Slaughter, *ACS Catal.* 2012, 2, 1802 – 1816.
- [34] A third resonance structure exists, which is similar to S7 but the double bond is localized between the carbon and the nitrogen atom bearing the tert-butyl group. Likely, the ligand effect will be the same, or proportional, for the two different C—N bonds.
- [35] C. L. Perrin, T. J. Dwyer, *Chem. Rev.* 1990, 90, 935 – 967.
- [36] These are the chlorine (complex 1), phosphines (complexes 4–6) and NHC (complex 9). See, for example: a) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* 2008, 108, 3351 – 3378; b) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* 2008, 37, 1776 – 1782.
- [37] The presence of tBu group in NH(tBu) moiety induces a sufficient hindrance to prevent cluster formation. Available X-ray structures do not show any specific Au—Au interaction. See ref. [32].
- [38] a) D. Zuccaccia, G. Bellachioma, G. Cardaci, G. Ciancaleoni, C. Zuccaccia, E. Clot, A. Macchioni, *Organometallics* 2007, 26, 3930 – 3946. For inter-ionic structures in solution of gold(I) complexes, see: b) G. Ciancaleoni, L. Belpassi, F. Tarantelli, D. Zuccaccia, A. Macchioni, *Dalton Trans.* 2013, 42, 4122 – 4131; c) D. Zuccaccia, L. Belpassi, L. Rocchigiani, F. Tarantelli, A. Macchioni, *Inorg. Chem.* 2010, 49, 3080 – 3082; d) D. Zuccaccia, L. Belpassi, F. Tarantelli, A. Macchioni, *J. Am. Chem. Soc.* 2009, 131, 3170.
- [39] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994, and references therein.
- [40] G. Ciancaleoni, N. Fraldi, P. H. M. Budzelaar, V. Busico, A. Macchioni, *Organometallics* 2011, 30, 3096 – 3105.
- [41] L. Rocchigiani, V. Busico, A. Pastore, A. Macchioni, *Angew. Chem. Int. Ed.* 2014, 53, 2157 – 2161; *Angew. Chem.* 2014, 126, 2189 – 2193.
- [42] H. Xu, W. H. Bernskoetter, *J. Am. Chem. Soc.* 2011, 133, 14956 – 14959.
- [43] The TEP is 2034.0 for Cl⁻, 2033.5 for Br⁻, 2033.6 for I⁻, 2051.5 for IPr, 2056.4 for PCy₃, 2068.9 for PPh₃, 2073 for Py, and 2071 cm⁻¹ for (C₆H₄F)₃P. Please, see refs. [4] and [44].
- [44] R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* 2005, 127, 2485 – 2495.
- [45] H. Haas, R. K. Sheline, *J. Chem. Phys.* 1967, 47, 2996 – 3021.
- [46] C. R. Landis, F. Weinhold, *J. Comput. Chem.* 2007, 28, 198 – 203.
- [47] N. Salvi, L. Belpassi, F. Tarantelli, *Chem. Eur. J.* 2010, 16, 7231 – 7240.
- [48] D. Zuccaccia, L. Belpassi, A. Macchioni, F. Tarantelli, *Eur. J. Inorg. Chem.* 2013, 4121 – 4135.
- [49] Our attempts to synthesize [(CO)Au(NAC)]⁺ failed, leading to the decomposition of the product.
- [50] Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, *J. Am. Chem. Soc.* 2014, 136, 6904 – 6907.
- [51] A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.* 2013, 49, 5541 – 5543.
- [52] G. Ciancaleoni, L. Biasiolo, G. Bistoni, A. Macchioni, F. Tarantelli, D. Zuccaccia, L. Belpassi, *Organometallics* 2013, 32, 4444 – 4447.
- [53] A. S. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* 2009, 694, 592 – 597.
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