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Comparative Theoretical Study of N-Heterocyclic Carbenes and Other Ligands Bound to Au^I

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Abstract: The bonding strength of N-heterocyclic carbene (NHC) ligands to a neutral AuCl test moiety are compared to that of several phosphanes and other ligands. Of the ligands studied, the NHCs clearly form the strongest bonds to AuCl. A simplified triangular CN_2 model is also introduced for the NHCs.

Keywords: carbenes · coordination chemistry · cyclopropenylidenes · gold · Lewis bases

Introduction

Qualitatively, the Fischer carbenes have a donor–acceptor interaction between the lone-pair electrons of the divalent carbon atom and the metal cation. This field of research was revitalized when Arduengo et al.[1] reported their stable N-heterocyclic carbene (NHC) imidazol-2-ylidene ligand. Many gold NHC compounds have been experimentally reported;[2–5] a minireview on carbenes was produced by Hahn.[6] A broad series of carbenes was compared in their complexation to Rh^I by Herrmann et al.[7] A very accurate study of the NHC itself and some light-element adducts has just appeared.[8]

Earlier calculations on NHC bonding to gold are not numerous. Boehme and Frenking[9] studied the trends along the series of coinage metals Cu, Ag, and Au and the main-group ligands carbene, silylene, and germylene. The strongest bond of 346 $kJ\,mol^{-1}$ indeed occurred in the case of NHC−AuCl. Both ionic and covalent contributions were found to be important, whereas little π back-bonding from the metal to the ligand was found. Nemcsok et al.[10] considered the $[(NHC)_2M]^+$ systems, for which Hu et al.[11] found both σ- and π-type bonding contributions. Sini et al.[12] found that the AuX ligands ($X = Cl$, NH_3^+, OH_2^+) prefer C to N binding in their interaction with imidazole. In other words, the NHC− mode is preferred to the alternative of N−Au complexation. Cyclic diphosphinocarbenes (PHC) is a related class of ligands that have been claimed to be even better σ donors than NHCs.[13]

To get a feeling for the position of NHCs in the broad series of ligands, particularly the phosphanes that they often replace, we report the present calculations in much the same way as did Schröder et al,[14] who ordered their ligands towards gas-phase Au^+.

Results

The calibration results are shown in Table 1 and the production results in Tables 2 and 3. The optimized structures of those species with nontrivial coordination are shown in Figure 1. The complexation energies of various ligands, L, to

Table 1. Calibration calculations on $Cl{-}Au{-}PH_3$.

Level[a]	Basis (RI)[b]	D_e [$kJ\,mol^{-1}$]	R(Au−Cl) [pm][c]
BP86	cc-pVDZ/ecp-60-mwb+2f	217	228.7
BP86(vert)	cc-pVDZ/ecp-60-mwb+2f	225	228.7
BP86(vert,cp)	cc-pVDZ/ecp-60-mwb+2f	220	228.7
RI-BP86	cc-pVDZ/ecp-60-mwb +2f(def-SVP)	217	228.6
RI-BP86	def-SVP(def-SVP)	204	230.0
RI-BP86	def2-TZVP(def-TZVP)	224	227.2
RI-BP86	def2-TZVPP(def-TZVP,def-TZVPP)	224	226.9
BP86	def2-QZVP	225	226.7
RI-MP2	cc-pVDZ/ecp-60-mwb+2f(cc-pVDZ,ecp-60-mwb-SVP)	266	225.9
RI-MP2	def2-TZVP(def-TZVP)	274	223.7
CCSD(T)	cc-pVDZ/cc-pVDZ-PP	201	227.4
CCSD(T)	cc-pVTZ/cc-pVTZ-PP	217	226.8
CCSD(T)	cc-pVQZ/cc-pVQZ-PP	229	226.0

[a] The symbol cp indicates counterpoise correction and vert indicates that the dimer geometries vere used for the free ligands. [b] The basis-set description A/B(C) refers to ligand elements A, gold basis B, and resolution-of-identity (RI) basis C. [c] Au−Cl bond length.

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Table 2. Calculated BP86/cc-pVDZ Au–L dissociation energies for the Cl–Au-L and Au^+–L series, Au–Cl and Au–L (nearest atom) distances, and two vibrational stretching frequencies and IR intensities for the Cl–Au–L series.

L	D_e(Au–Cl) [kJ mol^{-1}]	D_e(Au$^+$) [kJ mol^{-1}]	R(Au–L) [pm]	R(Au–Cl) [pm]	ν_{sym} [cm^{-1}] (I [km mol^{-1}])	$\nu_{antisym}$ [cm^{-1}] (I [km mol^{-1}])	Reference
NHC–Me	343		198.6	229.8	334 (14)	350 (23)	
NHC–H	340	557	197.2	229.4	275 (9)	346 (32)	
	371		197.6	229.6			[9] MP2
	346						[9] CCSD(T)
			198.6				[12]
NHC–Cl	321		196.9	228.9	224 (3)	348 (41)	
PHC–H	318	532	194.7	228.9	189 (17)	350 (64)	
PHC–N	306	499	193.4	228.3	194 (8)	354 (46)	
$C(PH_3)_2$	291	560	203.7	230.7	333 (33)	383 (9)	
CN–Me	280	410	190.1	224.6	344 (42)	382 (1)	
		297					[14]
P–Me_3	273	503	226.6	230.1	330 (51)	365 (0)	
PPh_3	260		227.4	230.3	190 (1)	337 (52)	
CO	244	261	188.3	225.2	371 (31)	482 (4)	
		201					[14]
PH_3	217	366	225.3	228.7	333 (35)	361 (2)	
		402					[14]
PF_3	213		219.6	226.6	231 (1)	360 (43)	
NH_3	213	342	209.5	226.5	355 (18)	446 (3)	
		297					[14]
pyridine	207		204.9	226.5	217 (2)	360 (31)	
triazine	187		204.1	225.8	217 (3)	366 (29)	
NC–Me	185	304	196.7	225.4	304 (13)	371 (17)	
		285					[14]
H_2S	170	295	231.1	227.7	295 (6)	355 (18)	
		230					[14]
H_2O	148	227	218.0	224.9	344 (0)	383 (25)	
		159					[14]
NF_3	129		201.0	223.9	227 (2)	379 (20)	
Xe	65	150	268.4	226.2	124 (0)	347 (16)	
		126					[14]

Table 3. Calculated BP86/cc-pVDZ results for some triangular 2π ligands bound to Au–Cl and Au^+.

L	D_e(Au–Cl) [kJ mol^{-1}]	D_e(Au$^+$) [kJ mol^{-1}]	R(Au–L) [pm]	R(Au–Cl) [pm]	ν_{sym} [cm^{-1}] (I [km mol^{-1}])	$\nu_{antisym}$ [cm^{-1}] (I [km mol^{-1}])
CP_2	324	499	192.0	228.1	255 (2)	352 (45)
C_3H_2	323	494	192.7	228.2	344 (41)	388 (0)
CN_2	281	341	190.1	225.9	356 (24)	395 (8)
N_3^+	268		190.3	219.2	338 (2)	424 (4)
NP_2^+	203	−155	193.1	221.0	247 (3)	400 (16)

the AuCl test particle are depicted in Figure 2. The main result is that, indeed, the three NHC ligands top the scale. A comparison with the complexation energies for a naked, gas-phase Au^+ cation is also made in both Tables 2 and 3 and Figure 2. Results for some 2π-aromatic ligands are summarized in Table 3.

Abstract in Swedish: Kvantkemiska beräkningar visar att N-heterocykliska karbener (NHC) bildar starkt bundna komplex med Au^I. I vår jämförelse av ett antal typiska ligander bundna till AuCl, uppvisar NHC den klart största bindningsstyrkan. Vi presenterar CN_2 som en förenklad model för NHC, och använder den för att i detalj analysera bindningen till AuCl.

Relativistic effects are important for gold. As an example, Boehme and Frenking[9] showed that half of the dissociation energy of (H-NHC)AuCl comes from relativistic effects. In the present work we did not perfom any nonrelativistic reference calculations.

Discussion

Our calculated order of ligand strength towards AuCl in Tables 2 and 3 is Xe $<$ NF_3 $<$ OH_2 $<$ SH_2 $<$ NC-Me $<$ pyridine $<$ NH_3, PF_3, PH_3 $<$ CO $<$ PPh_3 $<$ N_3^+, PMe_3 $<$ CN-Me, CN_2 $<$ $C(PH_3)_2$ $<$ PHC-H, NHC-Cl, C_3H_2, CP_2 $<$ NHC-H, NHC-Me. The order remains virtually unchanged for Au^+.

One remarkable NHC compound is the carbene-stabilized gold(I) fluoride of Laitar et al.,[15] which has an Au–F bond

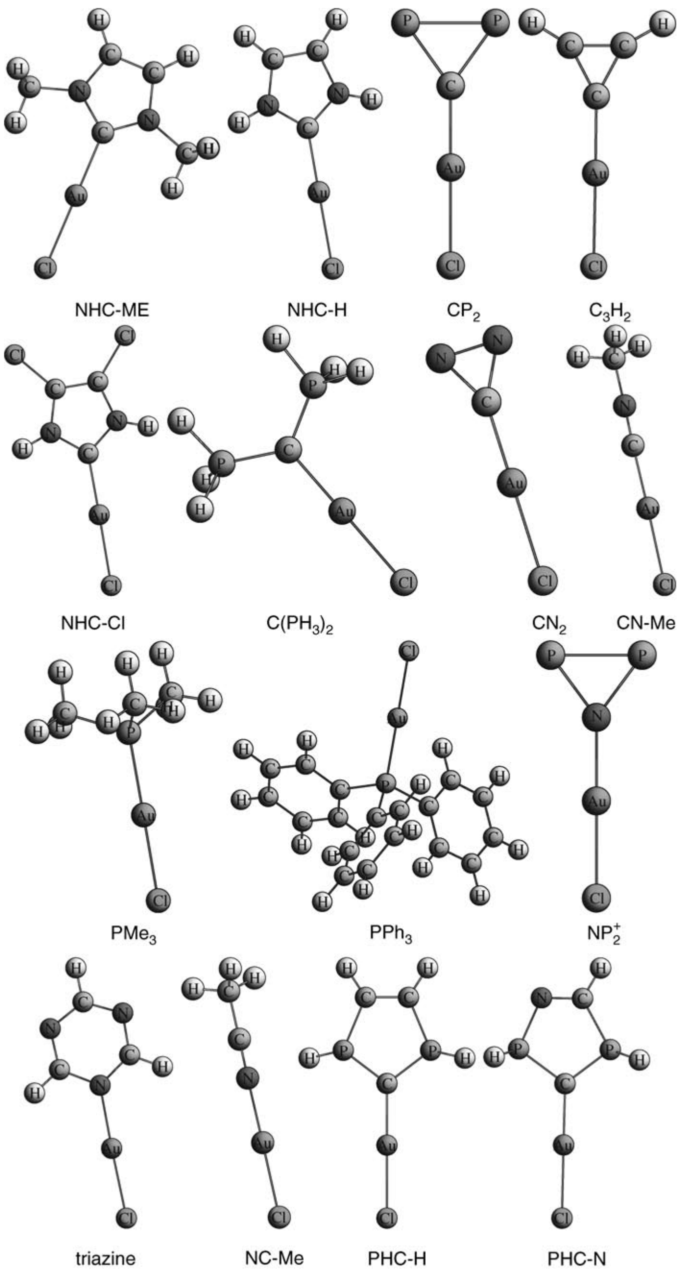

Figure 1. Optimized structures of the complexes studied.

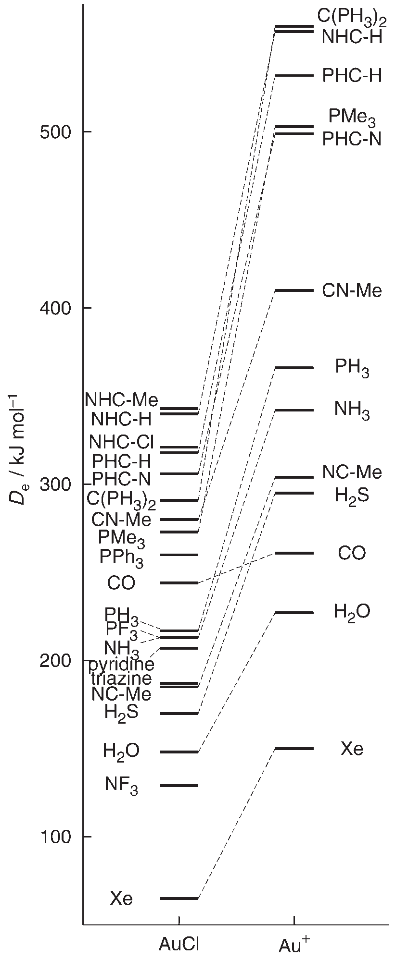

Figure 2. Calculated dissociation energies (D_e) at the BP86/cc-pVDZ level.

in a stable organometallic compound. Its experimental R-(Au−C) of 195.6 pm is in line with the Au−C bond lengths calculated herein. Similarly, the experimental Au−C bond lengths of Singh et al.[4] in a series of (NHC)AuCl compounds range from 193 to 203 pm; their group also quoted further data.

We studied the cyclic 2π-stabilized systems as a set of hypothetical model ligands, (Table 3). Here we introduced the triangular diazocyclopropene ligand CN_2 as a "baby model" for the NHC. It surpasses the phosphanes but not the NHCs in Au−L bond strength. For isolated CN_2, the cyclic singlet state lies above the linear triplet CNN state.[16–18] Notably, the diazirines also form excellent carbene precursors.[19] The calculated Au−C bond length for CN_2 is shorter than those for the NHCs, although the bond is weaker.

A pictorial analysis of the interaction between AuCl and the CN_2 baby model is shown in Figures 3 and 4. Starting with the σ interactions, 24A1 represents the main Au−C bond and 25A1 is dominated by N in-plane lone-pair electrons (right). 26A1 is another (slightly weak) example of a bond of the outer σ orbital on a transition metal, based on the s–dσ "doughnut" orbital. Such bonds are prominent in metalloactinyls, as discussed elsewhere.[20]

The off-plane π Au−C interaction is shared between 11B1 and 12B1, the latter also possessing a strong Cl 3pπ character. The in-plane π Au−C interaction is mainly in 12B2, with 13B2 being weakly Au−C antibonding.

Cyclopropenylidene, C_3H_2, which is isoelectronic to CN_2, is even more strongly bound than CN_2. Such cyclopropenylidenes exist in interstellar space, and the first laboratory results were only just published.[21] The Au−L bond strength is comparable to that of NHC−Cl. In matrix isolation spectroscopy, cyclopropenylidene was already observed by Reisenauer et al.[35] and Maier et al.[36]

The cyclic CP_2 could be considered as a simple model for cyclic diphosphinocarbenes. The Au−CP_2 bond-dissociation

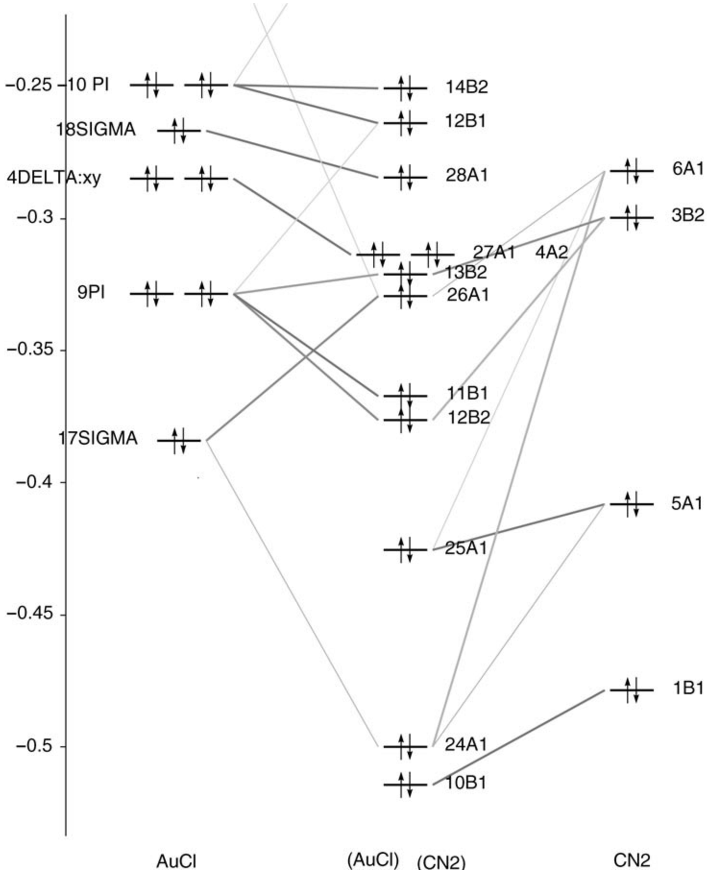

Figure 3. Orbital-correlation diagram for the (Cl−Au)(CN$_2$) complex.

energy is equal to that of Au−C$_3$H$_2$. Note that the bond strength of N$_3$$^+$ is comparable to that of PMe$_3$ despite the cationic character of gold in Au−Cl. Tarroni and Tosi found the cyclic singlet state (a′^{1} A$_1$) to be the first excited state for the isolated N$_3$$^+$.[22] The Brønsted basicity of carbodiphosphoranes is being studied computationally by Tonner and Frenking.[23]

We include in Table 3 the two vibrational Au−L stretching frequencies to characterize the Au−L bond for possible spectroscopic identification.

An energy-decomposition analysis[24] for five ligands is shown in Table 4. The repulsive Pauli part and the attractive electrostatic part roughly cancel. If we interpret the results that way, most of the net bonding, ΔE_{int}, could come from the orbital (covalent) interaction. Nemcsok et al.,[10] however, preferred to compare $\Delta E_{\mathrm{elstat}}$ against ΔE_{orb}. For NHC-Me and CN$_2$, the binding energy, $-\Delta E_{\mathrm{int}}$, of the latter is 63 kJ mol^{-1} smaller, although its Au−C bond length is 8.5 pm shorter. As seen in the two last columns of Table 4, $\Delta E_{\mathrm{Pauli}}$ and ΔE_{orb} is more favorable for CN$_2$ by 65 and

Table 4. Energy-decomposition analysis at the BP86/TZ2P level with the (Cl−Au)(L) fragments.

L	PH$_3$	PMe$_3$	NHC−H	NHC−Me	CN$_2$
ΔE_{int} [kJ mol^{-1}][a]	−229	−286	−325	−333	−270
$\Delta E_{\mathrm{Pauli}}$ [kJ mol^{-1}][b]	639	735	892	895	830
$\Delta E_{\mathrm{elstat}}$ [kJ mol^{-1}][c]	−595 (69 %)	−738 (72 %)	−920 (76 %)	−925 (75 %)	−721 (66 %)
ΔE_{orb} [kJ mol^{-1}][d]	−273 (31 %)	−283 (28 %)	−297 (24 %)	−302 (25 %)	−379 (34 %)
σ, π[e]	−185, −89		−212, 84		205, 174
q(AuCl)[f]	−0.0864	−0.1414	−0.1041	−0.1184	0.0741

[a] Total interaction. [b] Pauli interaction. [c] Electrostatic interaction; percentage of total attractive interaction in parentheses. [d] Orbital interaction; percentage of total attractive interaction in parentheses. [e] The separate σ and π contributions to ΔE_{orb}. [f] Hirshfeld charge[34] of AuCl fragment.

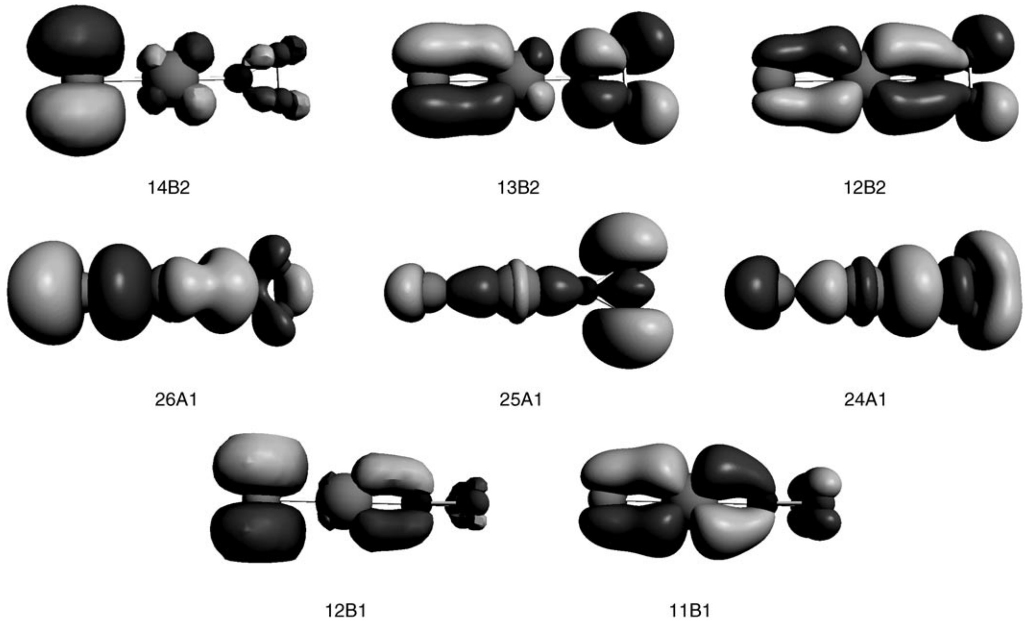

Figure 4. Representative molecular orbitals of the (Cl−Au)(CN$_2$) (left to right) complex. Orbitals of A1 and B2 symmetry are symmetric, whereas those of B1 are antisymmetric with respect to the molecular plane.

77 $kJ\,mol^{-1}$, respectively, but ΔE_{elstat} is less favorable by −204 $kJ\,mol^{-1}$.

Conclusions

1. In a comparing complexation to an AuCl test particle with other ligands, the NHCs have the largest complexation energies. The energies of complexation to Au^+ follow a closely similar trend.
2. The larger NHC−(AuCl) complexation energy relative to (ClAu)−PMe_3 is dominated by a larger electrostatic attraction, part of which is consumed against larger Pauli repulsion. The orbital interaction is only slightly larger.
3. A CN_2 baby model was introduced for the NHCs. Its Au−C bond length and binding energy are both smaller than those of the NHCs. However, it surpasses the phosphanes in Au−L bond strength.

Calculational Methods

Density functional calculations were performed by using the BP86 functional in conjunction with the cc-pVDZ basis sets, as implemented in Gaussian 03.[25] For gold, we used a 19-valence-electron scalar relativistic pseudopotential together with the corresponding (8s7p6d2f)/[6s5p3d2f] valence basis set.[26] For xenon, we used an 8-VE pseudopotential together with a (14s10p2d1f)/[3s3p2d1f] basis set.[27,28] Local minima on the potential-energy surface were verified by frequency analysis of the respective optimized geometry.

To investigate the effect of the computational methods on the results, we performed more-extended calculations on the Cl−Au−PH_3 system. These calculations were done at the DFT/BP86, MP2, and CCSD(T) levels together with basis sets of up to cc-pVQZ quality. These DFT/BP86 and MP2 calculations were performed within the RI approximation, as implemented in the TURBOMOLE program package.[29] The CCSD(T) calculations were done with the MOLPRO package,[30] in which we used the newly developed pseudopotential[31] and the corresponding correlation consistent basis sets on gold.[32] The calibration results are shown in Table 1. The dissociation energy obtained from a counterpoise-corrected calculation on Cl−Au−PH_3 at the BP86/cc-pVDZ level, in which the monomer geometries are fixed to that of the optimized dimer, differs by only a few percent from the uncorrected one. Hence, we expect the BSSE to be small.

If we take the results obtained at the CCSD(T)/cc-pVQZ level as a reference, we can conclude that the MP2 results exaggerate the bonding. The MP2 bond-dissociation energy is too large, and the Au−Cl bond length too short. With the exception of the smallest basis set, the SVP, the DFT/BP86 results are in reasonably good agreement with the reference data. A similar conclusion can also be made by comparing the results for NHC-H presented in Table 2.

The energy-decomposition analysis was done with the ADF program package.[33]

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