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Combining Ligand-Enhanced Backdonation and Steric Shielding to Stabilize a Mono-substituted Au(I) Carbene

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Abstract

A mono-substituted Au(I) carbene was prepared by reacting HC(N₂)(Dmp) (Dmp = 2,6-dimesitylphenyl) with an (*o*-carboranyl)-diphosphine AuNTf₂ complex. It is stable up to -10°C and was characterized by NMR spectroscopy. According to DFT calculations, the chelating P[^]P ligand enhances Au→C_{carb} backdonation, while the Dmp substituent provides kinetic stabilization but does not bias the electronic structure of the carbene complex.

Introduction

Many catalytic transformations involve gold(I) carbene complexes as key intermediates and these species attract considerable attention.¹ Important synthetic efforts have been devoted to the preparation and characterization of [L_nAu=C<]⁺ complexes² with various substitution patterns at the carbenic center (with and without heteroelements) and various ancillary ligands at gold (from phosphines, *N*-heterocyclic carbenes to diphosphines). See Chart 1 for representative examples of recently isolated and/or spectroscopically characterized compounds. The nature of the AuC_{carb} bonds also raises fundamental questions, with the cationic gold carbene Au⁺=C< and metala-carbocationic (carbenoid) Au-C<⁺ structures as limit canonical forms.³ Most of the gold(I) carbene complexes reported so far are disubstituted, but in 2019, Echavarren *et al* were able to observe monosubstituted gold(I) carbenes by NMR at -90°C.⁴ Here, gold bears JohnPhos-type ligands and the carbene center is substituted by a mesityl (Mes) group. These species are stable only until -70°C, but display rich reactivity.⁵

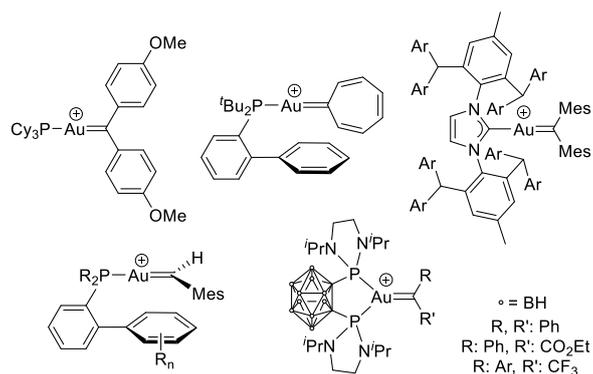


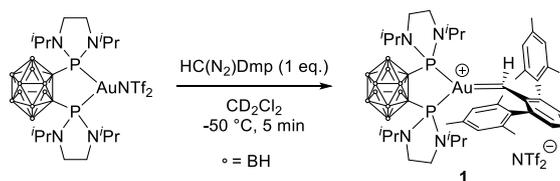
Chart 1. Representative examples of recently isolated and/or spectroscopically characterized $[L_nAu=C<]^+$ complexes.

Over the past few years, our group has demonstrated that (*o*-carboranyl)-diphosphines are very efficient in enhancing backdonation from gold (thanks to $P^{\wedge}P$ chelation) and stabilizing disubstituted gold(I) carbenes.^{2c,6} In this work, we envisioned to combine this approach with kinetic stabilization by a sterically demanding substituent. Hereafter, we report our first results along this line. A monosubstituted gold(I) carbene stable up to -10°C has been prepared and characterized by multi-nuclear NMR spectroscopy. Its bonding situation was analysed computationally.

Results and Discussion

As sterically demanding aryl substituent, we choose the 2,6-dimesitylphenyl (Dmp) moiety which has been successfully employed by Hillhouse *et al* to prepare low coordinate Ni complexes, (NHC)Ni(Dmp) and $(P^{\wedge}P)Ni=CH(Dmp)$ species in particular.^{7,8} The 2,6-dimesitylphenyl diazomethane $HC(N_2)Dmp$ was prepared in 4 steps from mesityl bromide and 1,3-dichlorobenzene in an overall yield of 32%.⁹ The reported synthesis^{8a} was modified and improved by replacing the highly toxic hydrazine and mercuric oxide for tosylhydrazine and sodium hydride.

Adding the pseudo-cationic $(P^{\wedge}P)AuNTf_2$ complex¹⁰ to $HC(N_2)Dmp$ at -50°C in dichloromethane resulted in a quick colour change from pale yellow-orange to deep purple (Scheme 1).



Scheme 1. Reaction of (P[^]P)AuNTf₂ with HC(N₂)Dmp resulting in the monosubstituted carbene **1**.

The monosubstituted carbene **1** was characterized by low-temperature multi-nuclear NMR spectroscopy (at -80 °C).⁹ A single peak at δ 141.3 ppm was observed in the ³¹P NMR spectrum, indicating a clean and quantitative reaction. The ¹H NMR spectrum shows a triplet at δ 13.36 ppm ($J_{\text{HP}} = 16.6$ Hz) for the AuCH(Dmp) moiety (Figure 1). This is approximately 1 ppm downfield shifted compared to the corresponding signal reported previously for the (JohnPhos)AuCH(Mes)⁺ complexes (δ 11.74 – 12.67 ppm).⁴ The ¹³C NMR resonance at δ 295.6 ppm (triplet, $J_{\text{CP}} = 85.6$ Hz) is also very diagnostic for the carbene complex **1**. It matches well with those found for the monosubstituted carbenes (δ 284.6 – 290.0 ppm).⁴ The correlation observed between the carbenic carbon and proton signals upon ¹H-¹³C HSQC analysis further confirms the assignment. The ¹H and ¹³C resonances associated with the Dmp moiety were assigned thanks to HSQC and HMBC experiments. The two mesityl groups were found to be inequivalent (two sets of signals were observed), indicating hindered rotation around the Au=C(H)(Dmp) bond.

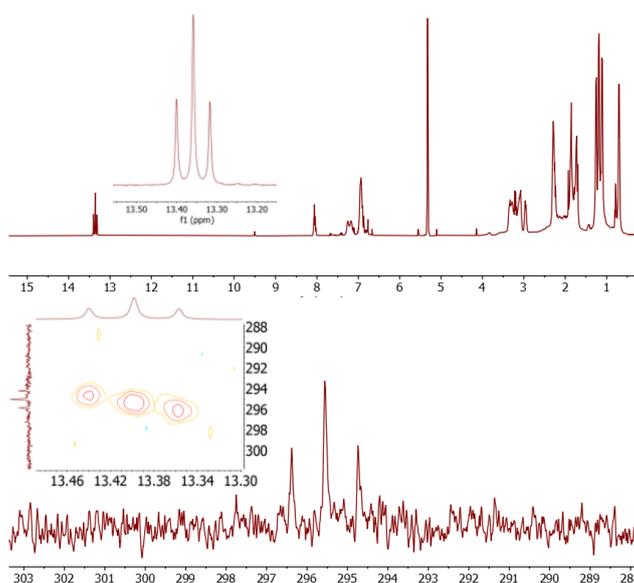


Figure 1. Top: ¹H NMR (400.13 MHz) spectrum of **1** with the Au=CH signal as inset. Bottom: ¹³C NMR (100.63 MHz) carbenic signal of **1** with the corresponding ¹H-¹³C HSQC correlation as inset. Spectra recorded in CD₂Cl₂ at -80 °C.

The thermal stability of **1** was then investigated. No colour change was observed when the (P[^]P)AuNTf₂ complex was added to HC(N₂)Dmp at -80 °C. When the solution was warmed, the

characteristic purple colour appeared at *ca* -60 °C and then disappeared at *ca* -10 °C. A variable temperature NMR monitoring was then carried out. A freshly prepared sample of **1** was analysed from -80 °C to room temperature by intervals of 10 °C.⁹ Accordingly, carbene **1** was found to survive up to -10 °C and to degrade completely within 5 minutes at 0 °C. The thermal stability of complex **1** substantiates the combined effect of Au \rightarrow C_{carb} backdonation (enhanced by the P[^]P ligand) and steric shielding (imparted by the Dmp substituent). The (JohnPhos)AuCH(Mes)⁺ complexes could be spectroscopically characterized at low temperature, but they were shown to decompose at temperatures between -90 and -70 °C.⁴

Despite our efforts, attempts to grow crystals suitable for XRD remained unsuccessful. To gain more insight into the structure and bonding situation of the (P[^]P)Au=CH(Dmp)⁺ complex, Density Functional Theory (DFT) calculations were carried out. The actual compound was considered, without simplification of the substituents, but the counter-anion was omitted. It is referred hereafter as **A-Dmp**. The B3PW91/SDD+f(Au), 6-31G^{**}(other atoms) level of theory was used to enable comparison with related complexes. The optimized structure (Figure 2, left) shows a tricoordinate gold complex (the two P atoms chelate the metal with a bite angle close to 90°). The carbene center sits in a planar environment which substantially deviates from trigonal due to the dissymmetric substitution pattern. The AuC_{carb}H bond angle is contracted while the AuC_{carb}C_{ipso} bond angle is widened at *ca* 108 and 144° , respectively (Table 1). The carbene plane is about perpendicular to the Au coordination plane, to minimize steric repulsions and maximize Au \rightarrow C_{carb} backdonation. Conversely, the phenyl ring of the Dmp moiety is coplanar with the carbene to accommodate the *o,o'*-Mes groups and enable π -donation to the vacant 2p(C_{carb}) orbital. The Au=C_{carb} bond length (1.975 Å) is comparable to those found in disubstituted (P[^]P)Au=C(R)(R')⁺ complexes.⁶ The C_{carb}–C_{ipso} bond length (1.428 Å) is similar to those found in (P[^]P)AuC(CF₃)(Ar)⁺ complexes, suggesting some π -stabilization of the carbene center.^{6c} The P[^]P ligand at gold and the Dmp substituent provide huge steric shielding. The central Au=CH moiety is protected by the P substituents on one side and the flanking Mes groups of the Dmp substituent on the other side, as apparent from the space filling model (Figure 2, right).

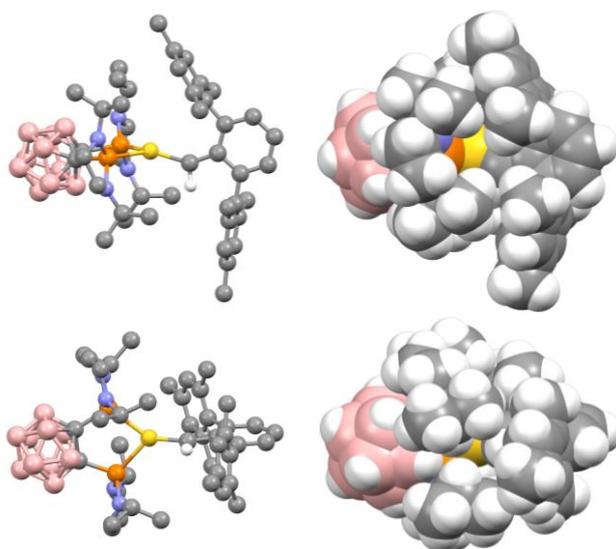


Figure 2. Optimized geometry (left) and space filling model (right) for the $(P^P)Au=CH(Dmp)^+$ complex **A-Dmp** at the B3PW91/SDD+f(Au), 6-31G**(other atoms) level of theory. Front (top) and side (bottom) views. Boron in pink, Phosphorus in orange, Nitrogen in blue, Gold in yellow, Carbon in grey, Hydrogen in white. For clarity, the hydrogen atoms are omitted in the optimized structures, except the one at the carbene center.

Inspection of the frontier orbitals shows some $Au=C_{carb}$ π -bonding as the result of $Au \rightarrow C_{carb}$ backdonation (Figure 3). The HOMO/LUMO correspond mainly to bonding/anti-bonding combinations between an in-plane $d(Au)$ orbital and the vacant $2p^\pi(\text{carbene})$ orbital. The HOMO/LUMO energy gap (2.64 eV) is comparable to those found in disubstituted $(P^P)Au=C(R)(R')^+$ carbenes (2.34–2.58 eV).⁶ In addition, a Natural Localized Molecular Orbital (NLMO) associated to the $Au \rightarrow C_{carb}$ backdonation evidences non-negligible mixing of the $2p^\pi(C_{carb})$ orbital with the $d(Au)$ -centered orbital (9.1 % C_{carb}), in line with some $Au=C_{carb}$ π -bonding.⁹

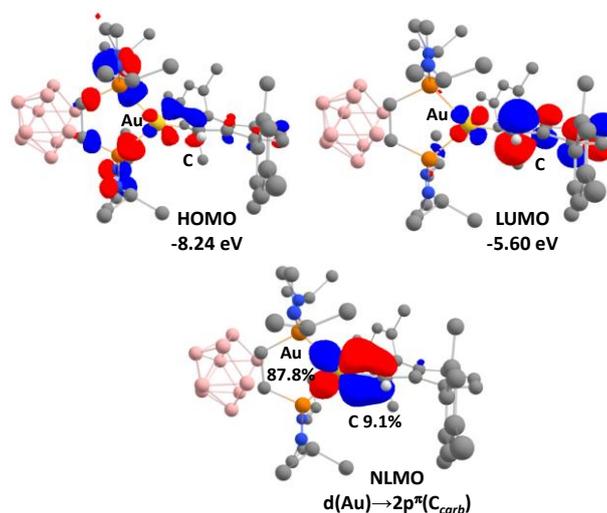
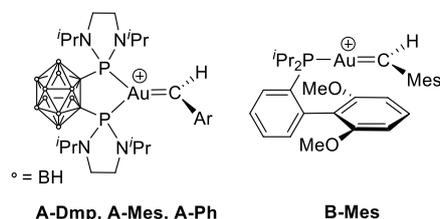


Figure 3. Frontiers orbitals (cutoff: 0.05) computed for the $(P^P)Au=CH(Dmp)^+$ complex **A-Dmp** at the B3PW91/SDD+f(Au), 6-31G** (other atoms) level of theory. NLMO (cutoff: 0.04) associated to the $Au \rightarrow C_{carb}$ backdonation with contribution in % of Au and C_{carb} atoms.

To further gauge the AuC_{carb} bonding, Natural Bond Orbital (NBO) analyses, Energy and Charge Decomposition Analyses (EDA and CDA) were performed (Table 1 & Table S4).⁹ Accordingly, the interaction between $(P^P)Au^+$ and $CH(Dmp)$ (both in the singlet state) turned to be the best fragmentation to describe **A-Dmp**. The charge transfer (CT) from the carbene center to the metal fragment was found close to zero (-0.03 e), while the donation/backdonation ratio (2.09) indicates the predominance of $C_{carb} \rightarrow Au$ donation, with significant $Au \rightarrow C_{carb}$ backdonation however.

Table 1 Key geometric features (bond distances in Å, bond angles in °) and bonding data computed for the (P[^]P)AuCH(Ar)⁺ complexes (Ar = Dmp, Mes, Ph) **A-Dmp**, **A-Mes**, **A-Ph**, as well as the reference (Johnphos)Au=CH(Mes)⁺ complex **B-Mes**.



	A-Dmp	A-Mes	A-Ph	B-Mes
Optimized structures				
Au=C _{carb}	1.975	1.979	1.959	2.007
PAu	2.458	2.429	2.422	2.378
	2.456	2.441	2.427	
C _{carb} –C _{ipso}	1.428	1.417	1.429	1.400
PAuP	88.94	89.44	89.14	-
AuCH	107.95	110.3	115.3	110.3
		0	7	2
AuCC _{ipso}	143.76	138.5	133.0	138.51
		5	4	
AuCC _{ipso} C _{ortho}	1.0	-5.0	1.2	-5.4
NBO analyses				
WBI(AuC _{carb})	0.754	0.727	0.768	0.681
WBI(C _{ipso} C _{ortho})	1.294	1.344	1.128	1.438
CT	-0.03	-0.02	-0.09	0.27
CDA analyses				
C _{carb} →Au donation	0.482	0.447	0.365	0.391
Au→C _{carb}	0.231	0.215	0.219	0.119
backdonation				
d/b ratio	2.09	2.08	1.67	3.29

We then questioned whether the steric shielding of the Dmp substituent influences the bonding situation or not. We tried to prepare the related $(P^{\wedge}P)Au=CH(Mes)^+$ complex by the same route, *ie* reacting $(P^{\wedge}P)Au(NTf_2)$ with $HC(N_2)Mes$. In this case, only diazo decomposition was observed and no gold carbene could be characterized. The carbenoid route employed by Echavarren *et al*⁴ to access the $(JohnPhos)AuCH(Ar)^+$ complexes was also tested but we could not find suitable conditions for the formal insertion of the carbene into the Au–Cl bond of the $(P^{\wedge}P)AuCl$ complex. Mixing $(P^{\wedge}P)AuCl$ with $HC(N_2)Mes$ only led to decomposition of the gold complex.¹¹

We thus resorted to DFT and performed calculations on the $(P^{\wedge}P)Au=CH(Mes)^+$ and $(P^{\wedge}P)Au=CH(Ph)^+$ complexes, **A-Mes** and **A-Ph**, respectively (Table 1). No significant difference was noticed between the optimized geometries of **A-Dmp**, **A-Mes** and **A-Ph**. The MO, NBO and CDA analyses also reveal very similar bonding situations. Thus, the huge steric hindrance of the Dmp substituent provides kinetic stabilization but does not bias the electronic structure of the carbene complex. Comparison with the complex **B-Mes** bearing a JohnPhos-type ligand is also insightful. The key geometric features do not differ much, but it is worth noting that the $Au=C_{carb}$ bond is longer (2.007 Å) while the $C_{carb}-C_{ipso}$ bond length is slightly shorter (1.400 Å). This suggests weaker $Au \rightarrow C_{carb}$ backdonation and stronger $Ar \rightarrow C_{carb}$ π -donation in **B-Mes** than in **A-Dmp**, as further supported by the respective Wiberg Bond Indexes (WBI). The CT value (0.27 e) and d/b ratio (3.29) found for **B-Mes** by NBO and CDA confirm this view and highlight the $Au \rightarrow C_{carb}$ backdonation enhancement induced by the chelating $P^{\wedge}P$ ligand.

Conclusion

In conclusion, a monosubstituted gold(I) carbene stable up to $-10^\circ C$ has been prepared thanks to the combined use of a chelating (*o*-carboranyl)-diphosphine ligand, to enhance $Au \rightarrow C_{carb}$ backdonation, and the sterically demanding Dmp substituent, to provide kinetic stabilization.

Future work will aim to extend this approach to other fleeting carbene complexes. Besides gold, it may be applicable to copper and silver, for which only few carbene complexes have been authenticated so far (Chart 2a).¹² Other exciting targets are the low valent complexes L_nMCR for which representatives of both the metalla carbene form and the carbyne complex have been recently reported (Chart 2b).¹³

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