Synthesis and structures of gold and copper carbene intermediates in catalytic amination of alkynes

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Metal carbenes are often proposed as reactive intermediates in the late transition metal-catalysed transformations of alkynes. Owing to their high reactivity, however, isolation and structural characterization of metal carbene intermediates in these transformations has remained unknown. Herein, we report the isolation of two acyclic gold and copper carbene intermediates in either Au(I)- or Cu(I)-catalysed cyclization of N-alkynyl formamidines through five-exo-dig cyclization. X-ray diffraction, 13C NMR spectra data and computational analyses provide evidence for the formation of a gold carbene intermediate with a carbocation-like electronic character. Using the intrinsic bond orbital (IBO) approach, we also evaluate the π-stabilizing effects of organic substituents at the carbene carbon atom in the gold carbene intermediate. Another rare six-membered copper carbene complex is also obtained through 6-endo-dig cyclization. These metal carbenes have proven reactive toward oxidation. The metal-promoted cyclization of N-alkynyl formamidine provides a facile approach to synthesize metal carbene species.

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late transition metal carbenes are widely proposed as active intermediate in many catalytic reactions\(^1\)\(^-\)\(^5\), and the most common metal carbenes are those prepared by decomposition of an appropriate diazo compound (Fig. 1a)\(^1\)\(^-\)\(^3\). The addition of nucleophilic agents to alkyne catalysed by late transition metals are of profound significance due to their high selectivity and mild conditions and has been investigated extensively for the synthesis of a variety of heterocycles and complex molecules\(^6\)\(^-\)\(^8\). Metal carbenes, in many cases converted from vinyl metal species, are often proposed as key intermediate in these transformation\(^8\)\(^,\)\(^10\). In the past 15 years, the transition-metal-catalysed cycloisomerization of ene-yne-ketones has been well established, and provides a safe, effective and practical alternative to the diazo decomposition route for metal carbene generation\(^11\)\(^-\)\(^23\). In the transformations, the metal π-activated alkyne is attacked by the carbonyl oxygen through 5-exo-dig cyclization to generate zwitterionic vinyl metal intermediate A that could be transformed into its resonance structure, metal (2-furyl)carbene intermediate B (Fig. 1b, \(M = \text{Cu}^{19,22}, \text{Au}^{18,23}, \text{Rh}^{13,15}, \text{Zn}^{17,18}\) and \(\text{Pd}^{20,21}\)). Metal carbene B subsequently undergoes a variety of transformations, such as oxidation, C-H insertion, cyclopropanation and heteroatom (N, O, Si, S)-H insertion reaction\(^1\)\(^-\)\(^23\). Recently, the groups of Zhang\(^18\) and Jiang\(^19\) reported that both Au(I) and Cu(I) (2-furyl)carbenes \((B \text{ with } M = \text{Au(I)} \text{ or } \text{Cu(I)})\) can undergo carbene oxidation to give 2-acyfluors (Fig. 1b). Like B, both Cu(I)-stabilized indazoylcarbene C reported by Haley group\(^24\)\(^-\)\(^26\) and Au(I) imidazopyridinylcarbene D reported by Cao group\(^27\) can also trap molecular oxygen to generate the corresponding 3-acylindazole or 3-acylimidazo-pyridine product, respectively. Owing to their high reactivity, however, isolation and structural characterization of late transition metal carbene intermediates in catalytic transformation of alkyne has remained unknown; information regarding the property of the metal carbene intermediates is limited to in situ NMR study and computational analysis\(^28\)\(^,\)\(^29\). Structurally characterized copper carbenes have been prepared only by either decomposition of the diazo precursors with various copper sources\(^30\)\(^-\)\(^33\) or carbene transfer from chromium complex\(^34\). On the other hand, several groups have successfully isolated a variety of structurally characterized gold carbenes\(^33\)\(^-\)\(^45\), but there remains an ongoing debate on the extent of the electronic character of gold carbenes as either carbene-like with a strong gold-to-carbon π-backbonding or carbocation-like with a weak π-backbonding\(^46\)\(^-\)\(^55\). Therefore, structurally characterized copper and gold carbenes, especially those involved in catalytic transformations, are highly desired for a clear understanding of the nature of gold carbenes and their essential role in the catalytic cycle.

As part of our long-standing interest in the design and synthesis of N-heterocyclic carbenes (NHCs) and abnormal NHC for catalysis, we previously reported the isolation of a rare vinyl silver species through 6-exo-dig cyclization of a formamidine with a σ,π-silver-activated terminal alkyne\(^56\). Herein, we first report the isolation and characterization of gold and copper carbene intermediates, E\(^(E = \text{Au(I)} \text{ or } \text{Cu(I)})\), in either Au(I) or Cu(I)-catalysed cyclization. Oxidation of formamidines with a internal alkyne through 5-exo-dig cyclization (Fig. 1c). In the presence of base, Cu(I)-promoted amination of a formamidine with a terminal alkyne leads to form a 6-membered copper carbene through 6-exo-dig cyclization. The carbene oxidation reaction of these metal carbene species are directly observed. The detailed structural and spectroscopic studies and computational analysis outline the nature of the gold and copper carbenes.

Results
Isolation of active copper carbene intermediates. First, phenyl-substituted formamidine 1 was initially examined in the amination cyclization (Fig. 2a). In the presence of a stoichiometric amount of IPrCuOTf (IPr = 2,6-bis(diisopropyl-phenyl)imidazol-2-ylidene), 1 underwent 5-exo-dig cyclization to form

\[ \text{CuLNR}_2 \]

Figure 1 | Selected metal carbene species involved in late transition metal-mediated transformations. (a) Late transition metal carbenes generated by decomposition of the diazo precursors. (b) Proposed late transition metal carbenes in catalytic cycloisomerization of alkyne. (c) Gold and copper carbene intermediates isolated in gold- and copper-catalysed cyclization of N-alkynyl formamidines.
a 5-membered vinylcopper species 2 at 10 °C in 82% yield, while raising the reaction temperature to 60 °C resulted in 6-endo-dig cyclization to afford a 6-membered vinylcopper species 3 in 53% isolated yield. Hydrolysis of either 2 or 3 with HOTf gave the corresponding cyclic formamidinium salt 4 or 5, respectively. In the presence of a catalytic amount of IPrCuOTf and one equivalent of trifluoromethanesulfonic acid (HOTf), the cyclization of the protonated formamidine 1 was required at elevated temperature to achieve a good yield (90%), forming a 5-membered product 4. The structures of 4 and 5 were confirmed by X-ray diffraction analysis (see Supplementary Figs 26 and 27).

The Cu-mediated cyclization of formamidine 1 seems to be kinetic versus thermodynamic control reaction. However, attempts to form 3 by heating 2 failed. Vinlylcopper species 2 has proven stable only in the solid state at room temperature, and is quite sensitive to oxidation in solution. The formation of a zwitterionic compound 6 was observed from the CDCl3 solution of 2 on standing 1 week (Fig. 2b). Compound 6 represents a zwitterionic precursor for a kind of hybrid ambidentate NHC ligand decorating the classical imidazol-2-ylidene with an acetlyacetonato unit. Further investigation showed 6 can also be directly obtained via cyclization of 1 using a catalytic amount of IPrCuOTf and H2O2 as oxidant at 25 °C in 57% isolated yield. When using CuBr·Me2S (10 mol%) as catalyst, 6 could be formed in air with a considerable yield (83%). The structure of 6 was confirmed by X-ray crystallography (Fig. 3a), showing it contains a conjugated backbone of alternating single and double bonds of type C1–C2 = C3–C16 = O2 as evidenced by comparison of bond distances within the acac backbone.

The transformation of either vinylcopper species 2 or alkynyl formamidine 1 into 6 is reminiscent of the observation of the carbene oxidation products of both copper (2-furyl)carbene B (M = Cu) and copper pyrazolylcarbene C in the Cu-catalysed cyclization of alkynes (Fig. 1b). Based on the observations, the transformation of 2 into 6 would be better described as a copper carbene oxidation reaction (Fig. 2b). The 13C NMR analysis of 2 exhibits one signal for the carbene carbon at δ = 211.4 p.p.m., which is similar to the imidophosphamidato copper α-carbonyl carbene signal at δ = 219.0 p.p.m., upfield of that for the diketiminato copper carbene (δ = 253.1 p.p.m.)31, and fall into the approximate range of 200–400 p.p.m. established for the very deshielded terminal carbene complexes. It is more deshielded than the carbene signal of IPr moiety in 2 at 181.9 p.p.m. The observation verifies the presence of an electrophilic carbene in 2. Vinylcopper 3 is quite stable in solvent and substantially inert to oxidation. The 3 is colourless, and copper carbene 2 is purple. Similarly, both imidophosphamidato copper α-carbonyl carbenes and diketiminato copper carbene complexes31 are all violet or purple. It indicates that the presence of a β-carbonyl in 2 is crucial for generating a copper carbene intermediate.

After massive attempts to isolate single crystals of 2 failed, we managed to obtain a single crystal of its IPr* counterpart carbene 7 suitable for X-ray diffraction analysis (Figs 3b and 4a). Copper carbene 7 was prepared as a wine red solid from the cyclization of 1 in the presence of one equivalent of IPr*CuNTf2, which could also catalyse the transformation of 1 into 6. The direct oxidation of 7 to form 6 was also observed in an oxygen atmosphere. In complex 7, the C-O bond distance of 1.207(7) Å is characteristic for a C=O double bond. The imidazol-4-one ring in 7 is essentially planar, indicating charge delocalization. The observation suggests the imidazol-4-one ring in 7 could be regarded as a mesoionic imidazolium-4-olate (Fig. 4b). The related mesoionic compounds have been known for several decades, and a similar 1,2,3-triazolium-4-olate compound G was reported by Albrecht and co-workers. Therefore, copper complex 7 could be described as a copper carbene complex bearing a mesoionic imidazolium-4-olate ring. The Cu1-C1 bond (1.924(6) Å) in 7 is similar to that (1.882(3) Å) for a three-coordinate cationic copper carbene.
\[ \text{[Cu(=CR^1(OR^2)](MeCN)(OEt_2)]^+} \quad (R^1 = (E)-CH=CH-2-furyl; R^2 = menthyl)^{34}, \text{and longer than those (1.822–1.834 Å) observed for the copper carbene obtained from either diphenylidiazomethane or \( \alpha \)-carbonyl diazo compounds}\]^{30–33}. The imidazolium-4-olate ring in 7 is nearly co-planar with the carbene centre, and the neighbouring phenyl ring is tilted with a slightly contracted bond (1.470(8) Å) between the carbene centre and the \( C_{ipso}(\text{Ph}) \) carbon.

**Isolation of active gold carbene intermediate.** Since gold carbenes are also reactive towards carbene oxidation\(^{16,27}\), we further investigate gold-catalysed cyclization oxidation of 1. Delightfully, in the presence of a catalytic amount of \( \text{PPh}_3\text{AuOTf} \) (10 mol%) and using \( \text{H}_2\text{O}_2 \) as oxidant, 6 could be obtained in 43% yield (Fig. 5a). Treatment of a stoichiometric amount of \( \text{PPh}_3\text{AuOTf} \) with 1 offered gold carbene 8 as a yellow solid in 60% yield. In the presence of \( \text{H}_2\text{O}_2 \), 8 underwent oxidation to give...
The carbene carbon of 8 in the 13C{1H} NMR spectra appears as a doublet at δ = 208.6 p.p.m. (JCP = 103.0 Hz), which is upfield of the carbene carbon resonance of those known gold carbene complexes (δ = 225–321 p.p.m.)35–44, and downfield of that for IPrAuCl (δ = 175.1 p.p.m.)60. The formation of 8 was unequivocally confirmed by X-ray crystallography (Fig. 6).

Recently, several groups have reported the isolation of gold carbene complexes 9 (ref. 42), 10 (ref. 41), 11 (ref. 37), 12 (refs 35,36) and 13 (ref. 35), which could be stabilized by π conjugation of the electrodeficient carbene centre with heteroatoms (Fig. 5b). The Au–C1 bond (2.044(9) Å) in 8 is similar with those found in the gold carbene complexes 12 and 13 (2.039–2.046 Å)35,36, and longer than those in gold carbene complexes 9–11 (2.010–2.032 Å)37,41,42 and non-heteroatom- but diaryl-stabilized gold carbene complexes (1.984(4)–2.014(6) Å) 38,40. Like 7, the mesoionic imidazolium-4-olate ring in 8 is nearly co-planar with the carbene centre, which enables efficient π-orbital overlap.

DFT computation and IBO analysis on gold carbene intermediate.

Similar to their copper counterparts, structurally characterized gold carbenes have been mainly prepared by either decomposition of the diazo precursors with various gold sources or carbene transfer from chromium complexes 35–45. Isolation and structural characterization of gold carbene intermediates generated from the addition of nucleophilic agents to C=C multiple bonds remains very rare. In 2008, the Hammond group 61 reported the spectroscopic detection of a gold carbene/oxonium complex 14 in the gold-mediated cyclization of allenoate and later the Hashmi group 62 isolated the gold carbene intermediates of type 14 and carried out density functional theory (DFT) calculation to study the bonding properties (Fig. 7). Very recently, Mouries-Mansuy, Fensterbank and colleagues 63 isolated and structurally characterized a related gold carbene 15 in the gold-mediated cyclization of pyridyl-allene.

The Au–C bond distance of 1.984(2) Å for 15 with a chloride ligand is shorter than that (2.049(9) Å) for 8, and is in the low range of those known gold carbenes35–45 (Fig. 7). It should be noted that, in contrast to π-acidic phosphine ligand, the π-donating chloride ligand could increase gold-to-carbon

Figure 5 | Preparation of gold carbene 8 and related heteroatom-stabilized gold carbenes 9–13. (a) Au-catalysed cyclization oxidation of N-alkynyl formamidine 1 and gold carbene intermediate 8. (b) Heteroatom-stabilized gold carbenes 9–13.

Figure 6 | Molecular structure of 8 with 20% probability. The counterion (OTf−) and H atoms in aryl rings have been omitted for clarity.
bonding, resulting in a short Au–C bond. The gold carbene signal of a related PPh₃-ligated gold carbene in the ¹³C{¹H} NMR spectrum appears at δ = 203.9 p.p.m., which is similar to that for 8.

Next, we performed DFT calculations to get more insight into the bonding property in 8. All the DFT calculations were performed using Gaussian 09 suite of programs. The TPSS functional with Grimme’s D3-BJ correction for van der Waals interaction was utilized in combination with the triple-ζ basis set def2-TZVPP (see Supplementary Methods for more details). The optimized geometry parameters of 8 are in line with the experimental results. Based on the Mayer bond order analysis (Fig. 7), partial single bond for C₂–C₁ can be formulated in the vinylgold complex 8. Similar bonding scenario was also observed for the related gold complexes 15 (ref. 63) and 14 (ref. 62).

The intrinsic bond orbital (IBO) analysis is a novel method to analyze chemical bonding. The IBOs mainly depict occupied orbitals in an intuitive way, assigning proportionally the electrons in the doubly occupied IBOs to the individual atoms and allowing quantitative interpretation of chemical bonding. Quite recently, using DFT and the IBO approach, Hashmi, Kastner and colleagues evaluated the π-stabilizing effects of organic substituents at the carbene carbon atom in several recently isolated and characterized gold carbene complexes, and the observations by the IBO method are consistent with the previously proposed bonding scenario for the gold carbene species. Therefore, we further carried out the IBO approach to study the π-stabilizing effects of organic substituents in gold intermediate 8.

As depicted in Fig. 8, we identified a strong π-stabilization in 8, which is mainly achieved through the π system of the imidazolium-4-olate ring attached to C¹ (Fig. 8d). Additionally, small contribution from the phenyl ring attached to C¹ was also identified. The phenyl ring is polarized towards C₁, forming the delocalized π bonding with C¹. In addition, the IBO of coordinative bond between the lone pair of carbene C¹ and the gold atom was identified (Fig. 8a) since this IBO is...
mainly located at C\textsuperscript{1}. The IBO representing the filled d orbital at gold aligned for p backbonding was also identified but it is largely located at gold atom up to 96.8\% (Fig. 8c), suggesting little contribution to stabilize carbenic C\textsuperscript{1}. Therefore, gold carbene intermediate \textit{8} should be better described as gold- and heteroatom-stabilized carbocation \textit{8}' (Fig. 5).

Very recently, we isolated a related vinylgold complex \textit{16} prepared by reacting IPrAuOTf with a formamidine bearing a terminal alkyne moiety\textsuperscript{56}, which could undergo protodeauration to afford a bis(hydroxylimidazol)ium salt (Supplementary Fig. 22). Different from gold carbene \textit{8}, \textit{16} is quite stable in air, while treatment of \textit{16} with excess H\textsubscript{2}O\textsubscript{2} resulted in complex reaction mixtures without clear product identified. We also reported a PPh\textsubscript{3} counterpart of \textit{16}, which is prone to undergo aurophilicity to form a vinyl gem-digold species\textsuperscript{64}. The observations suggest besides the imidazolium-4-olate ring, a phenyl substituent bonding to the carbenic carbon, is also important to stabilize gold carbene \textit{8}. The differences in reactivity between gold species \textit{8} and \textit{16} may possibly imply the gradation in character from carbene to vinylgold species.

**Isolation of six-member copper carbene species.** In a stoichiometric AgOTf-promoted cyclization of formamidine \textit{17} bearing a terminal alkyne, we previously revealed that presence of a base can preclude the protonation of imino moiety by HOTf, thus changing cyclization fashion\textsuperscript{56}. Moreover, Hashmi \textit{et al.}\textsuperscript{55,66} also reported that addition of a base can slow down the protodemettallation to conserve organometal species.

The observations inspired us to investigate the influence of base in the copper-promoted amidiniumation of \textit{17}. Delightfully, treatment of \textit{17} with CuBr.Me\textsubscript{2}S in the presence of N(iPr)\textsubscript{2}Et\textsubscript{2} as a base afforded a 6-membered vinylcopper species \textit{18} as a yellow solid in a 6-endo-dig cyclization fashion (Fig. 9). Treatment of \textit{18} with AgOTf in the presence of PPh\textsubscript{3} resulted in the formation of a divinylcopper species \textit{19} as a yellow solid, the structure of which was confirmed by X-ray crystallography (Fig. 10). The Cu–C bond (1.870(9) Å) in \textit{19} is shorter than that (1.924(6) Å) for copper carbene \textit{7}. In addition, the Cu–C distance in \textit{19} is shorter than those for IPrCuCl (1.953(8) Å)\textsuperscript{67}, and the related (IPr\textsubscript{2}Cu)\textsuperscript{+}BF\textsubscript{4} (1.926(19) Å, 1.938(18) Å)\textsuperscript{68}, and similar to those for either mesoionic NHC imidazol-5-ylidene copper complex (1.871(7) Å)\textsuperscript{69}, or abnormal NHC triazol-5-ylidene copper complex (1.876 (4) Å)\textsuperscript{69}. In the \textsuperscript{13}C\{1H\} NMR spectra, the carbene carbon resonates at \(d = 194.5\) p.p.m. for \textit{18} and \(d = 193.7\) p.p.m. for \textit{19} are similar to the lower range of those established for terminal carbenes (\(d = 200–400\) p.p.m.)\textsuperscript{58}, and downfield of those for imidazol-5-ylidine copper complex (\(d = 159.5\) p.p.m.) and triazol-5-ylidine copper complex (\(d = 166.4\) p.p.m.)\textsuperscript{69}. Interestingly, similar to the five-membered copper carbene complex \textit{2}, \textit{18} is also found to be reactive towards oxidation in solution. A zwitterionic oxo-adduct \textit{20} was isolated from the DCE solution of \textit{18} on stirring for 1 day, indicating that vinylcopper species \textit{18} is more like a copper carbene complex \textit{18}' which also contains a β-carbonyl. Therefore, we speculate that the reason why the six-membered vinylcopper \textit{3} does not react as a copper carbene is largely because of the presence of an
x-carbonyl instead of a β-carbonyl in 2 and 18. Zwitterionic compound 20 is known as a zwitterionic precursor for an aminocarbene.\(^7\)

**Discussion**

We have developed both Au(I)- and Cu(I)-catalysed cyclization oxidation of N-propiolic formamidines through 5-exo-dig cyclization. Key gold and copper carbene intermediates are isolated from the stoichiometric reaction, which were fully characterized. X-ray diffraction analysis and \(^{13}\)C NMR spectra data provide evidence for the formation of a gold carbene intermediate with a carbocation-like electronic character. Using DFT and the IBO approach, we evaluated the π-stabilizing effects of organic substituents at the carbene carbon atom in the gold carbene complex 8. In the presence of base, Cu(I)-promoted amidination of the formamidine with a terminal alkyne leads to form a six-membered copper carbene through 6-endodig cyclization. The generation of these gold and copper carbene complexes is attributed to the presence of a β-carbonyl group, and their oxidation reactions are directly observed. The metal-promoted cyclization reaction of N-alkynyl formamidines also provides a facile approach to synthesize metal carbene species, and our future efforts are directed at synthesizing other metal species by using the facile method.

**Methods**

**General.** Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in p.p.m. from tetramethylsilane with the solvent as the internal standard (\(^1\)H NMR CDCl\(_3\): 7.26 p.p.m.; \(^{13}\)C NMR CDCl\(_3\): 77.0 p.p.m.). Synthetic procedures for compounds 1c, 2–6 and 18–20 are summarized in Supplementary Methods. For NMR analysis and X-ray structures of the compounds in this article, see Supplementary Figs 1–21. For more details, please see also Supplementary Methods.

**Synthesis of copper carbene complex 7.** The mixture of formamidine 1 (100 mg, 0.20 mmol) and \(\text{IPr}^*\text{CuNTf}_2\) (205 mg, 0.20 mmol) was stirred in the 1,2-dichloroethane (DCE; 3 ml) at 10 °C for 30 min. All volatiles were removed under vacuum, and the residue product was washed twice with diethyl ether to afford pure 7 as a wine red solid (260 mg, 74%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.07\) (s, 1H), 7.64 (t, \(J = 7.9\) Hz, 1H), 7.40 (d, \(J = 7.9\) Hz, 2H), 7.17-7.07 (m, 19H), 7.02-6.97 (m, 3H), 6.90-6.84 (m, 14H), 6.76 (d, \(J = 7.6\) Hz, 7H), 6.71 (s, 4H), 6.45 (t, \(J = 6.8\) Hz, 1H), 6.27 (t, \(J = 7.6\) Hz, 2H), 5.80 (d, \(J = 7.6\) Hz, 2H), 5.48 (s, 2H), 5.20 (s, 4H), 2.83-2.76 (m, 2H), 2.74-2.65 (m, 2H), 2.15 (s, 6H), 1.33 (d, \(J = 6.8\) Hz, 6H), 1.27-1.18 (m, 12H), 1.13 (d, \(J = 6.8\) Hz, 3H), 1.05 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 215.41, 181.18, 163.28, 151.88, 145.91, 144.13, 143.18, 142.38, 140.81, 140.19, 139.46, 134.48, 131.66, 129.99, 129.55, 129.43, 129.38, 129.18, 128.68, 128.43, 128.06, 126.79, 126.55, 126.24, 124.80, 124.57, 124.41, 123.69, 29.62, 29.22, 25.96, 24.36, 23.62, 21.84; 31P NMR (162 MHz, CDCl\(_3\)) 140.93, 134.16, 131.66, 131.17, 129.60, 129.16, 127.12, 125.70, 125.27, 124.61, 124.21, 121.89, 29.62, 29.22, 25.96, 24.36, 23.62, 21.84; \(^{18}\)O NMR (162 MHz, CDCl\(_3\)) \(\delta = 39.52\). HRMS (MALDI): m/z [M-NTf\(_2\)]\(^+\) calcd. for C\(_{36}\)H\(_{36}\)CuN\(_2\)OP\(_2\): 1467.6880; found: 1467.6895.

**Synthesis of gold carbene complex 8.** The mixture of PPh\(_3\)AuCl (99 mg, 0.20 mmol) and silver triflate (51 mg, 0.20 mmol) was stirred in the DCE (1.5 ml) at 25 °C for 15 min, and then the solid components were filtered off and the filtrate was added to the solution of 1 (100 mg, 0.20 mmol) in the DCE (1 ml). After stirring for 1 h at 25 °C, all volatiles were removed under vacuum. The residue product was washed twice with diethyl ether to afford pure 8 as a yellow solid (132 mg, 63%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 10.19\) (s, 1H), 7.56-7.47 (m, 10H), 7.46-7.39 (m, 6H), 7.35 (d, \(J = 7.9\) Hz, 3H), 6.96 (d, \(J = 7.9\) Hz, 2H), 6.93-6.83 (m, 5H), 2.84-2.67 (m, 4H), 1.39-1.26 (m, 18H), 1.22 (d, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 208.56\) (d, \(J_{\text{C-P}} = 103.0\) Hz), 162.98, 155.86, 145.75, 145.42, 140.93, 143.16, 131.66, 131.17, 129.60, 129.16, 127.12, 125.70, 125.27, 124.61, 124.21, 121.89, 29.62, 29.22, 25.96, 24.36, 23.62, 21.84; \(^{18}\)O NMR (162 MHz, CDCl\(_3\)) \(\delta = 39.52\). HRMS (MALDI): m/z [M-OTf\(_2\)]\(^+\) calcd. for C\(_{36}\)H\(_{36}\)AuN\(_2\)OP\(_2\): 1915.3718; found: 1915.3699.

**Data availability.** The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1418063 (4), CCDC 1418064 (5), CCDC 1499714 (6), CCDC 1470533 (7), CCDC 1470532 (8) and CCDC 1449046 (19). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All data are available from the authors on reasonable request.
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Author contributions

J.W., S.L. and C.Z. performed the synthetic experiments. X.C. performed DFT calculations. J.Z. conceived of metal carbene design and reactivity applications. J.Z., M.S. and S.X. designed the project. J.Z. and J.W. wrote the manuscript.

Additional information

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