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Preparation of *Remote* NHC Complexes of Rhodium(I) and Gold(I) by Ligand Transfer

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The *r*NHC complexes (5-butyl-1,2-dimethylpyridin-4(1*H*)-ylidene)$Cr(CO)_5$ (**1**), as well as the novel compounds (1,2-dimethyl-5-phenylpyridin-4(1*H*)-ylidene)$M(CO)_5$ (**2**, M = Cr; **3**, M = W) and (1-methylpyridin-4(1*H*)-ylidene)$Cr(CO)_5$ (**7**) were prepared from Fischer carbene complexes. Reaction of **1** with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ then afforded the first *r*NHC Rh^I complex, **4**. Transfer of the ligand in **2** to Ph_3PAu^+ afforded the cationic *r*NHC gold complex, **5** and reaction of **3** and **7** with [AuCl(tht)] gave the neutral *r*NHC–AuCl complexes **6** and **8**. The compounds were characterised by IR and multinuclear NMR spectroscopy as well as mass spectrometry. The crystal and molecular structures of the *remote* pyridinylidene complexes **3**, **4**, **5**, **6** and **8** were determined by single-crystal X-ray diffraction.

Introduction

During the past 10 years N-heterocyclic carbenes (NHCs)[1] have claimed their place alongside phosphanes, as a most important group of ligands to stabilise and activate metals during homogeneous catalysis.[2] Initially, the subgroup of these ligands that have become part and parcel of mainstream organic chemistry because being adopted in the second-generation Grubbs catalyst[3] and commercialised by Aldrich following important work by Organ,[4] were based on imidazole or other azole ligands with, in most instances, the carbene carbon generated in the 2-position of the two-N, five-membered rings (the so-called *normal* position of the N^2HC^5). More recently, the so-called *abnormal*[5,6] N^2HC^5s were discovered and developed. In such imidazolylidenes, the carbene carbon is found in position 4 of the alkylated imidazole ring.

Simultaneously, interest in one-N six-membered carbenes (N^1HC^6s) derived from pyridinium salts, with the first examples already reported by Stone in 1974,[7] has grown with the preparation of group 10 metal complexes and their utilisation in C,C-coupling catalysis.[8]

The latter complex types are *normal* (carbene in *ortho* position 2) or *remote* (carbene in *para* position 4). A number of calculations have also been carried out to describe the carbene–metal bonding.[9] In another contribution to the present special edition,[10] these calculations are significantly extended for the pyridinylidenes and related families to also include complexes of the *abnormal* type (also *remote* – carbene carbon in the *meta* position 3) as well as *remote* quinolinylidene ligands with the carbene carbon outside the N-heterocyclic ring. It is of particular interest in the context of this paper that *r*N^1HC^6 complexes of gold are not known[11] – *normal* pyridin-2-ylidene (*n*N^1HC^6) complexes of Au^I have been made from 2-bromopyridine by lithiation, transmetallation and protonation.[12]

The standard method to prepare *remote* pyridinylidene complexes of the transition metals involves oxidative substitution, typically applicable to group 10 metal systems that can be isolated as phosphane complexes in their zero oxidation states but also exhibit stable M^{II} oxidation states. A similar approach cannot be used for group 6 metals but Aumann,[13] when reacting α,β-unsaturated mono-alkylamino carbene complexes, $[M\{=C(OMe)CH=C(R^1)\text{-}NHR^2\}(CO)_5]$, with alkynes, prepared such products in satisfactory yields by ring closure. No crystal structure determination was reported. We have recently discovered a new method to make the required (aminovinyl)carbene complexes of chromium and tungsten.[14]

In this contribution we report on the extension of Aumann's ring closure as well as carbene transfer from group 6 metals onto rhodium and gold fragments to form a number of unique new compounds.

Results and Discussion

Synthesis

The compounds **1**–**3** were synthesised according to a somewhat modified procedure of Aumann in 20–63% yield.[13] Classic Fischer-type carbene complexes,

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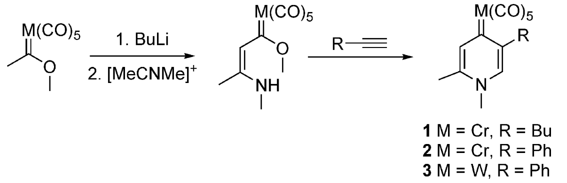
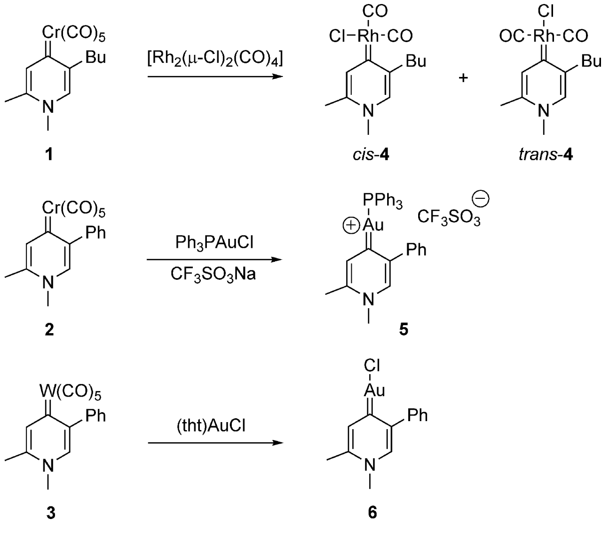
$[M\{=C(OMe)Me\}(CO)_5]$ (M = Cr or W), were converted into α,β-unsaturated $[M\{=C(OMe)CH=C(R^1)NHR^2\}(CO)_5]$ compounds by treatment with butyllithium and an *N*-methylacetonitrilium salt[14] before ring closure using suitable alkynes (Scheme 1). The facile conversion of Fischer-type carbenes into *r*NHCs emphasises the close relationship between these two classes of compounds.



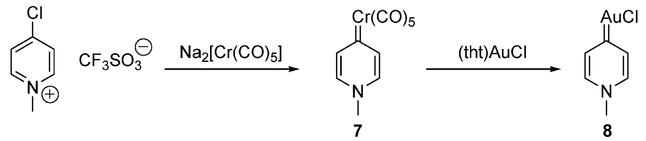
Scheme 1. Formation of *r*NHC complexes **1**–**3** in two steps from Fischer-type carbene complexes.

*r*NHC transfer to Rh^I was readily effected by reacting the group 6 complex **1** with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in a CH_2Cl_2 solution to produce a mixture of the *cis*- and *trans*-isomers of **4** (Scheme 2) in 56% and 44% yield, respectively. Crystallisation of *trans*-**4** was not achieved – the equilibrium might shift towards the *cis* isomer during crystallisation. Geometric isomerism in Rh^I complexes has been observed,[15] albeit related nN^2HC^5-analogues of **4** have only been isolated when being *cis*-disposed.[16] For the transfer reactions to Au^I a *r*NHC ligand with a phenyl substituent was synthesised to avoid thermal motion associated with the alkyl chain that had been observed in the crystals of **4** (vide infra). Other transfers were achieved either by reacting the chromium complex, **2** with $[AuCl(PPh_3)]$ and CF_3SO_3Na in acetonitrile or by reaction of the tungsten complex, **3** with [AuCl(tht)] (tht = tetrahydrothiophene) in thf to respectively form compounds **5** and **6** (Scheme 2) in 78% and 71% yield, respectively.



Scheme 2. Transfer of *r*NHC ligands in **1**–**3** to Rh^I or Au^I.

Because the simpler *r*NHC ligand, 1-methylpyridin-4(1*H*)-ylidene, is not accessible by the same procedure, the pyridinylidene complex **7** was synthesised in 11% yield by slight modification of a procedure developed by Stone[7] and portrayed in Scheme 3. The related gold complex **8** was then obtained by transmetallation with [AuCl(tht)] in 27% yield. The gold complexes **5**, **6** and **8** exhibited markedly lower solubilities than the respective starting compounds and other products, thus facilitating their easy separation. Compound **5** is soluble in acetonitrile and CH_2Cl_2 while **8** is only slightly soluble in acetone; the solubility of **6** is low in all three solvents.



Scheme 3. Formation of the *r*NHC compound **7** according to Stone[7] and subsequent carbene transfer to Au^I.

Characterisation

Infrared Spectroscopy

For all octahedral complexes of Cr and W four bands $[A_1^{(1)}, B_1, E$ and $A_1^{(2)}]$ for the vibration modes of the transition metal pentacarbonyl unit are expected (although B_1 is theoretically infrared inactive, it does appear owing to distortion of the ideal C_{4v} symmetry around the metal). The B_1, E and $A_1^{(2)}$ bands in the spectra of **1**, **2**, **3** and **7** overlap or are closely grouped together as a result of the band broadening observed when the spectra of compounds are measured in CH_2Cl_2,[17,18] but the strong $A_1^{(1)}$ and very strong E bands are clearly observed in all instances. The fact that the $A_1^{(1)}$ band for **1** appears at a much lower frequency (2040 cm^{-1}) than its precursor, $[Cr\{=C(OMe)–CH=C(NHMe)Me\}(CO)_5]$ (2052 cm^{-1})[13,14] indicates that the carbene ligand in **1** transfers more electron density to the metal than the acyclic complex.

Because frequencies of the carbonyl vibrations are sensitive to the electron density on the metal coordinated to them; a comparison of the CO stretching frequencies of complexes **1**–**3**, **4** and **7** with those of analogous classical $M–N^2HC^5$ (M = Cr for **1**, **2** and **7**, W for **3** and Rh for **4**) complexes allows a qualitative estimation of the donor strength of the pyridin-4-ylidene compared to the imidazol-2-ylidene ligand.[19,20] This method was utilised by Herrmann et al.[21] and Bertrand and co-workers[22] for a variety of carbenes. As indicated above, a higher CO frequency in general corresponds to a lower electron density on the metal as affected by the σ-donation and π-acceptor ability of the chosen ligand (when ignoring possible stereoelectronic effects). It is believed that pyridinylidene ligands are stronger σ-donors than imidazolylidene ligands as shown by DFT calculations performed in Frenking's group,[9] and would therefore effect lower ν(CO) values. The $A_1^{(1)}$ and E bands of **1** (2040, 1911 cm^{-1}), **2** (2041, 1916 cm^{-1}), **3** (2052, 1914 cm^{-1}) and **7** (2044, 1917 cm^{-1}) indeed all appear at lower frequencies than the same bands in imidazol-2-ylidene complexes of Cr (ca. 2056 and 1924 cm^{-1}) and W (ca. 2064 and 1922 cm^{-1}).[20] Two stretching bands are observed for the CO ligands in *cis*-**4** (2046, 1983 cm^{-1}). From a comparison of the ν(CO) frequencies for *cis*-**4** to those of *cis*-bromo(dicarbonyl)(1-ethyl-3-methyl-2,3-dihydro-1*H*-imidazol-2-ylidene)rhodium (2079 and 2000 cm^{-1}; no solvent specified) and *cis*-chloro(dicarbonyl)[(*tert*-butyl)(diisopropylamino)methylidene]rhodium[22] (2057 and 1984 cm^{-1}; considered to contain a very basic ligand; no solvent specified), it can be concluded that pyridin-4-ylidene exhibits a significantly larger σ_d/π_a ratio than the two mentioned ligands. Only one band is observed for the CO ligands in *trans*-**4** (1915 cm^{-1}).

Mass Spectrometry

For complexes **1** (*m*/*z* 355), **2** (*m*/*z* 375), **3** (*m*/*z* 507) and **7** (*m*/*z* 285) the molecular ion peaks and the typical fragmentation of carbonyl carbene complexes originating from consecutive CO ligand loss are detected. Although the molecular ions of the rhodium carbene complexes *cis*-**4** and *trans*-**4** are not observed, fragments corresponding to Cl (*m*/*z* 322), 2 × CO (*m*/*z* 302) as well as concurrent Cl and 2 × CO (*m*/*z* 264) losses are present. The *r*NHC gold complexes show an [M – Cl]$^+$ base peak (*m*/*z* 380 for **6** and 290 for **8**) while **8** also forms an interesting Cl-bridged dinuclear ion, [(carbene)Au(μ-Cl)Au(carbene)]$^+$ (*m*/*z* 615), in the mass spectrometer. Ionic **5** yields the cation as the base peak (*m*/*z* 642) accompanied by [AuPPh$_3$]$^+$ (*m*/*z* 459) and [AuL]$^+$ (*m*/*z* 380).

NMR Spectroscopy

All the expected signals for the new compounds are present. The signals for the protons and the carbons of the pyridinylidene ring were assigned according to assignments made as a result of ^{1}H-NOE and ^{13}C, ^{1}H-shift correlation NMR experiments performed by Aumann and co-workers on [5-butyl-1-methyl-2-phenylpyridin-4(1*H*)-ylidene]pentacarbonylchromium.[13] The differences in the proton chemical shift between the H-2/6 and H-3/5 protons as well as the corresponding ^{13}C chemical shift differences of the adjacent carbon atoms C-2/6 and C-3/5 are significantly smaller in the *r*NHC rhodium and gold complexes (^{1}H, $\Delta\delta$ 0.4 in **4**, **5** and **8** and only $\Delta\delta$ 0.03 in **6**; ^{13}C, $\Delta\delta$ ca. 10 in **4**, $\Delta\delta$ ca. 0.4 in **5**, **6** and **8**) compared to the group 6 *r*NHC compounds (^{1}H, $\Delta\delta \approx 1.3$ and ^{13}C, $\Delta\delta \approx 16$ for **1**–**3** and **7**). Additionally, the ^{1}H signals for the *C*-methyl and *N*-methyl groups in complexes **4**–**6** and **8** are observed at higher field than for the starting materials. The proton NMR signals of *trans*-**4** always appear at a somewhat lower field strength than those of *cis*-**4**.

It was possible to extract $^1J_{C,H}$ coupling constants from the ^{13}C-satellite signals of the sharp resonances of the *r*NHC ligand in **5**.

All the signals for the carbene complexes in their ^{13}C NMR spectra can be assigned and appear in the expected relative positions. The highest $C_{carbene}$ resonances are seen in the *r*NHC complexes of the group 6 metals, **1**–**3** and **7** (δ = 232.5, 238.0, 218.9 and 241.2 ppm, respectively) whereas the values for the comparable gold analogues, **5**, **6**, and **8** (δ = 199.5, 186.5 and 185.3 ppm) are found upfield by up to 56 ppm. The signals for $C_{carbene}$ of the rhodium complexes *cis*- and *trans*-**4** (δ = 211.0 and 209.2 ppm) also appear significantly upfield from the same signals in their Cr and W analogues.

The $C_{carbene}$ resonance of the *r*NHC complex **1**, appears 52.5 ppm upfield when compared to its precursor, the Fischer carbene [Cr{=C(OMe)CH=C(NHMe)Me}(CO)$_5$], and this effect can be ascribed to the loss of the electron withdrawing O atom adjacent to the carbene carbon. All other signals for **1** appear downfield when compared to its precursor with the exception of the signal for $C_{carbene}$ and the signal for CCH$_3$.

The CO carbon *cis* to the carbene ligand in the rhodium compound, *cis*-**4**, resonates at δ = 186.1 ppm and the one *trans* to the carbene ligand at δ = 192.2 ppm, both signals are doublets. This assignment is based on the difference in *trans* influence of the chloride and carbene ligands respectively. With the carbene ligand exhibiting a larger *trans* influence than the chloride ligand, the ^{103}Rh–^{13}C coupling constant for the doublet assigned to the *trans*-CO carbon ($^1J_{Rh,C}$ = 54.9 Hz) should be smaller than that for the doublet assigned to the *cis*-CO carbon ($^1J_{Rh,C}$ = 79.7 Hz), as is indeed the case. The signal for the carbene carbon atom of *cis*-**4** appears as a doublet at δ = 209.2 ppm ($^1J_{Rh,C}$ = 29.9 Hz). This signal for the carbene carbon has a smaller coupling constant than that of the CO ligands because the latter have a larger *trans* influence than the carbene ligand and far greater than the chloride ligand. These assignments are consistent with the Rh^I complexes with N^{2}HC^5 ligands reported by the group of Crabtree.[16b] The signals for the carbene carbons of *cis*-**4** and *trans*-**4** are very similar. The coupling constant for the carbene carbon of *trans*-**4** is 2 Hz larger than in *cis*-**4** because the carbene ligand is located *trans* to the chloride. Only one signal (δ = 188.3 ppm) is observed for the CO ligands in *trans*-**4** because they occur in the same chemical environment; because of their greater mutual *trans* influence they have a smaller Rh–C coupling constant ($^1J_{Rh,C}$ = 50.9 Hz).

The signals for the *trans*- and *cis*-CO groups in the *r*NHC carbene complex **3** are observed at ca. δ = 206 and 203 ppm, respectively, with typical $^1J_{W,C}$ coupling constants of 130 Hz. For the carbene complexes of Cr the *trans*- and *cis*-CO signals appear at δ = 226 and 220 ppm. The signal for the *ipso*-C of the phenyl rings of the PPh$_3$ ligand in **5** overlap with the signal of the *meta*-C of these rings.

Compound **5**, which features a triphenylphosphane ligand, shows one singlet ^{31}P NMR resonance (δ = 41.8 ppm) at a lower field than that of [AuCl(PPh$_3$)] (δ = 33.0 ppm).[23]

Crystallography

No crystal and molecular structures of tungsten, rhodium or gold *r*NHC complexes are known and the new complexes **3**–**6** and **8** were now also studied by X-ray diffraction. Compound **3** shown in Figure 1 exhibits the expected octahedral geometry around the tungsten centre. The largest deviation from linearity for a given set of mutually *trans*-located ligands occurs between two CO groups [C22–W1–C24 170.7(2)°]. The pyridinylidene ring forms an angle of 26.5(2)° with the plane containing C21, C22, C24 and W1, thus resembling an intermediate between a staggered and eclipsed configuration with the $W(CO)_3$ fragment. The effect of the *r*NHC ligand on the W–CO_{trans} distance [2.003(4) Å] in **3** is comparable to that of the related *n*N^1HC^6 complexes of tungsten where the distances were found to be 1.993 Å in one as well as 2.014 and 2.007 Å for two asymmetric molecules in another complex.[24] The W–$C_{carbene}$ distances of the latter complexes, 2.277(5) Å as well as 2.287 and 2.285 Å, are also comparable to the same distance in **3** [2.271(4) Å]. The interplanar angle of the phenyl group with the pyridinylidene ring [68.8(2)°] in **3** is larger than in the *r*NHC gold complexes [48.9(2)° in **6** and 43.3(3)° in **5**] reflecting the higher steric demand of the $W(CO)_5$ group. Compared to its immediate synthetic precursor $[M\{=C(OMe)CH=C(R^1)NHR^2\}(CO)_5]$[14] (cf. Scheme 1), the W1–C4 and C4–C5 bonds are of similar length, the C5–C6 bond [1.416(4) and 1.377(5) Å for the precursor and **3**, respectively] is shortened and the N1–C6 bond elongated [1.319(4) vs. 1.355(3) Å].

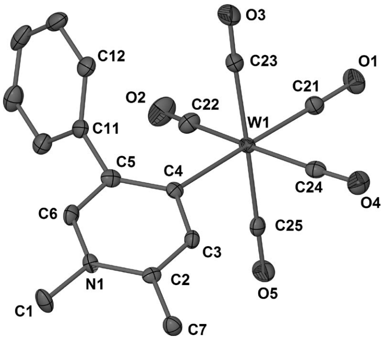


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: W1–C4 2.271(4), W1–C21 2.003(4), W1–CO_{cis} 2.034 (average), C4–W1–C21 176.1(2), C22–W1–C24 170.7(2), C23–W1–C25 178.0(2).

The rhodium *r*NHC complex **4**, crystallised as the hemihydrate of the *cis*-isomer shown in Figure 2. The Rh^I centre exhibits square-planar geometry, the plane of its coordination sphere and the pyridinylidene ring lie at an angle of 75.2(2)°. No N^1HC^6 complexes of rhodium are known; only compounds that carry the 2,3,5,6-tetrafluoro-4-pyridyl ligand, thus formally representing unalkylated "precursors" to *r*NHC complexes, have been described. Differences between $4{\cdot}0.5H_2O$ and *trans*-carbonyl(2,3,5,6-tetrafluoropyrid-4-yl)bis(triethylphosphane)rhodium[25] are the C–$C_{carbene}$–C angles, 116.5(5)° and 111.7(1)°, respectively, the Rh–C bonds to the heterocyclic ligand [2.092(2) Å in the fluoropyridine complex] as well as the Rh–CO_{trans} bonds [1.849(2) Å in the tetrafluoropyridyl complex compared to 1.931(6) Å in $4{\cdot}0.5H_2O$], highlighting the larger *trans*-influence of the *r*NHC ligand compared to the tetrafluoropyridyl group. The *trans*-effect of the *r*NHC ligand is also reflected in the respective Rh–CO bond lengths within $4{\cdot}0.5H_2O$ which show a discrepancy of ca. 0.1 Å. A water molecule is trapped in a cavity at a special position with twofold rotation symmetry, causing the hemihydrate stoichiometry. Lacking a hydrogen bond to stabilise its position, it exhibits strong thermal motion; such movement is also shown by the adjacent terminal methyl group of the butyl side chain.

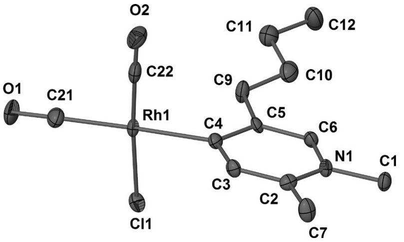


Figure 2. Molecular structure of $4{\cdot}0.5H_2O$; co-crystallised water is not shown. Selected bond lengths [Å] and angles [°]: Rh1–C4 2.067(5), Rh1–C21 1.931(6), Rh1–C22 1.813(6), Rh1–Cl1 2.382(2), C4–Rh1–C21 177.7(2), Cl1–Rh1–C22 175.9(2), Cl1–Rh1–C4 88.2(2), C22–Rh1–C4 87.8(2).

The Au–C bond [2.049(3) Å] of cationic complex **5** (Figure 3), is significantly longer than in the neutral *r*NHC gold chloride compounds **6** [1.991(7) Å] and **8** [1.979(6) Å] and comparable to those found in the two asymmetric molecules of the cationic N^2HC^5 complex [1,3-di-*tert*-butylimidazol-2-ylidene](triphenylphosphane)gold(I) hexafluorophosphate [2.044(4) and 2.034(4) Å], showing the *trans* influence of PPh_3,[26] as well as in the N^1HC^6 bis(pyridin-2(1*H*)-ylidene)gold(1+) cation [2.03(2) and 2.02(2) Å].[12] The Au–P distance in **5** [2.2888(8) Å] is somewhat longer than the same distances in the imidazol-2-ylidene compound [2.275(1) and 2.274(1) Å] in turn highlighting the greater *trans* influence of the *r*N^1HC^6 ligand. The PPh_3 ligand in **5** is engaged in a sixfold phenyl embrace[27] with another cation related by a centre of inversion between the phosphorus atoms (P–P′ distance 6.745 Å, symmetry operator 2 – *x*, 2 – *y*, 1 – *z*).

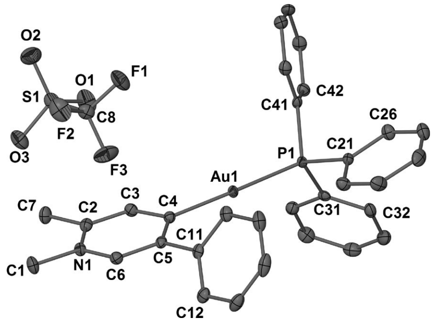


Figure 3. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Au1–C4 2.049(3), Au1–P1 2.2888(8), P1–Au1–C4 176.92(9).

In the molecular structure of the substituted *r*NHC complex **6**, (Figure 4), the Au–C as well as Au–Cl bond lengths are similar to the values found in the unsubstituted **8**. The Au–Cl bonds in **6** and **8** [2.304(2) and 2.314(2) Å] are longer than in $[AuCl(PPh_3)]$ [2.279(3) Å][28] but roughly comparable to the same separation in chloro(pyrazolin-3-ylidene)-gold complexes [2.307(2) and 2.299(2) Å].[29] It came as somewhat of a surprise that the crystal structure of **8**, shown in Figure 5, consists of discrete molecules, devoid of any close sub-van der Waals interactions. Given the low steric demand of the 1-methylpyridin-4(1*H*)-ylidene ligand, this complex seemed a natural candidate for Au···Au interactions. Indeed, as no such interactions were found in any of the *r*NHC gold complexes reported here, further studies are needed to determine whether this is an incidental result or has intrinsic electronic causes.

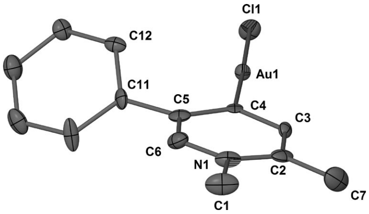


Figure 4. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Au1–C4 1.991(7), Au1–Cl1 2.304(2), Cl1–Au1–C4 178.7(2).

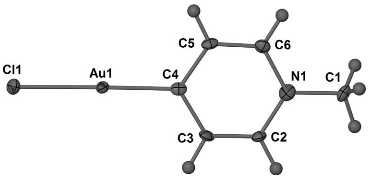


Figure 5. Molecular structure of **8**. Selected bond lengths [Å] and angles [°]: Au1–C4 1.979(6), Au1–Cl1 2.314(2), Cl1–Au1–C4 179.1(2).

Upon inspection of the respective bond lengths within the pyridinylidene ligands of complexes **3**–**6** and **8**, no significant trends can be observed here that would give insight into the relative contributions of the formally neutral pyridin-4(1*H*)-ylidene and the charge-separated 4-pyridylium resonance structures in the complexes of different metal fragments. Bond lengths in the ligand seem to be relatively insensitive to the different ratios of contributing resonance structures involved, M–$C_{carbene}$ bonds certainly are.[30]

Conclusions

One-N six-membered *r*NHC complexes of chromium and tungsten were made from α,β-unsaturated Fischer carbene complexes, prior to successful metal exchange with gold(I) and rhodium(I) complex fragments. Based on the comparison of CO vibrations in compound **4** with those in NHC rhodium(I) complexes, it is clear that pyridin-4-ylidene ligands are stronger electron donors than their imidazol-2-ylidene counterparts. The compounds containing the softer metals Rh^I and Au^I also consistently show smaller ^{13}C chemical shifts for the carbene carbons than those observed in the group 6 metal complexes. The *r*NHC complexes have been characterised by single-crystal X-ray diffraction constituting the first such study involving tungsten, rhodium and gold complexes.

Experimental Section

General: All work was performed under dry argon using standard Schlenk and vacuum-line techniques. All solvents were distilled under dry dinitrogen,[31] CH_2Cl_2 and MeCN were distilled from CaH_2, pentane, hexane and toluene from sodium and diethyl ether and thf from sodium wire and the sodium benzophenone ketyl radical. Methyllithium was standardised prior to use.[32] Supplied chemicals were used without further purification. Flash chromatographic separations[33] were performed with double walled columns that were cooled down to –15° with "flash grade" Florisil (200–300 mesh) or silica gel 60 (230–400 mesh) under inert atmosphere. The dimensions of the columns refer to adsorbent height × column diameter.

Instrumentation: ^1H, ^{13}C, and ^{31}P NMR spectra (ppm) were recorded with Varian VXR 300, Varian VNMRS 300, Varian Unity Inova 400 or Varian Unity Inova 600 instruments. ^1H (300/400/600 MHz) and ^{13}C NMR (75/101/151 MHz) spectra were referenced relative to residual solvent peaks. ^{31}P NMR (121/162/243 MHz) spectra were referenced externally to 85% H_3PO_4. IR spectra were recorded at 4 cm^{-1} resolution on a Nicolet Avatar 300 FT-IR instrument equipped with a Smart Performer ZnSe disk ATR accessory or a Perkin–Elmer 1600 Series. The spectra were corrected for ATR effects using Omnic software supplied with the spectrometer. FAB mass spectra were recorded in (nitrophenyl)-methanol matrices on a VG 70 SEQ mass spectrometer at the University of the Witwatersrand. Melting points were determined on a Stuart Scientific SMP3 instrument or on a Fischer Scientific (Pittsburgh PA, St. Louis MO) and Eimer & Amend (New York, NY) hot stage apparatus and are uncorrected. Elemental analyses were performed at the University of Cape Town or the University of the Witwatersrand.

Synthesis of the Compounds

Starting Materials: The starting materials $[M\{=C(OMe)Me\}(CO)_5]$,[34] M = Cr or W, $[MeCNMe][BF_4]$[35] and [AuCl(tht)][36] were prepared according to the literature procedures.

Synthesis of 1: The method described by Aumann et al.[13] was utilised to obtain a yellow microcrystalline product of **1** (0.152 g, 0.428 mmol) from $[Cr\{=C(OMe)CH=C(NHMe)Me\}(CO)_5]$ (0.207 g, 0.678 mmol)[14] and 1-hexyne (0.139 g, 0.19 mL, 1.70 mmol). Yield 63%, 0.15 g, m.p. 114 °C (dec.). ^1H NMR (CD_2Cl_2): δ = 8.41 (s, 1 H, CCH), 7.17 (s, 1 H, NCH), 3.80 (s, 3 H, NCH_3), 3.08 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.46 (s, 3 H, CCH_3), 1.56 (m, 4 H, $CH_2CH_2CH_2CH_3$), 0.98 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 232.5 (s, $C_{carbene}$), 226.1 (s, CO_{trans}), 221.0 (s, CO_{cis}), 153.7 [s, C(*n*Bu)], 146.9 (s, CCH), 135.5 (s, CCH_3), 131.4 (s, NCH), 43.3 (s, NCH_3), 38.9 (s, CCH_3), 34.1 (s, $CH_2CH_2CH_2CH_3$), 22.9 (s, $CH_2CH_2CH_2CH_3$), 18.8 (s, $CH_2CH_2CH_2CH_3$), 14.1 (s, $CH_2CH_2CH_2CH_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 2040 [m, $A_1^{(1)}$], 1911 (s, *E*), 1882 [m, $A_1^{(2)}$] cm^{-1}. MS (FAB): *m*/*z* (%) = 355 (5) $[M]^+$, 327 (6) $[M - CO]^+$, 289 (15) $[M - 2\,CO]^+$, 272 (5) $[M - 3\,CO]^+$, 243 (11) $[M - 4\,CO]^+$, 215 (7) $[M - 5\,CO]^+$. $C_{16}H_{17}CrNO_5$ (355.33): calcd. C 54.1, H 4.8, N 3.9; found C 54.5, H 5.0, N 4.1.

Synthesis of 2: The compound was prepared by the same method as described for **1** from $[Cr\{=C(OMe)CH=C(NHMe)Me\}(CO)_5]$ (1.20 g, 3.93 mmol) and ethynylbenzene (1.2 g, 0.93 mL, 9.11 mmol). The R_f values of **2** and its precursor pentacarbonyl-[(*Z*)-3-(methylamino)-1-methoxybut-2-en-1-ylidene]chromium are virtually identical. Yield 32% (based on the last alkyne addition step), 0.47 g, m.p. 130 °C (dec.) ^1H NMR ($CDCl_3$): δ = 8.74 (s, 1 H, CCH), 7.50 (m, 5 H, Ph), 7.38 (s, 1 H, NCH), 3.96 (s, 3 H,

NCH_3), 2.67 (s, 3 H, CCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 238.0 (br. s, C_{carbene}), 225.7 (s, CO_{trans}), 219.9 (s, CO_{cis}), 155.1 (s, CPh), 147.0 (s, C*C*H), 143.3 (s, *C*CH_3), 134.7 (s, *i*-Ph), 130.9 (s, NCH), 129.9 (s, *o*-Ph), 128.2 (s, *m*-Ph), 127.9 (s, *p*-Ph), 42.7 (s, NCH_3), 18.8 (s, C*C*H_3) ppm. IR (ATR): $\tilde{\nu}_{\nu(CO)}$ = 2036 [s, $A_1^{(1)}$], 1958 (sh, B_1), 1871 [vs, E and $A_1^{(2)}$] cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 2041 [s, $A_1^{(1)}$], 1957 (sh, B_1), 1916 [vs, E and $A_1^{(2)}$] cm^{-1}. MS (FAB): *m*/*z* (%) = 375 (10) [M]$^+$, 347 (16) [M – CO]$^+$, 263 (23) [M – 4 CO]$^+$, 235 (19) [M – 5 CO]$^+$. $C_{18}H_{13}CrNO_5$ (375.30): calcd. C 57.6, H 3.5, N 3.7; found C 57.7, H 3.7, N 3.5.

Synthesis of 3: Compound **3** was prepared in the same fashion as **1** from [W{=C(OMe)CH=C(NHMe)Me}$(CO)_5$] (2.01 g, 4.50 mmol) and ethynylbenzene (1.2 g, 1.3 mL, 11.8 mmol). The R_f values of **3** and its precursor are virtually identical. Yield 20% (based on last alkyne addition step), 0.48 g, m.p. 178 °C (dec.). ^1H NMR ($1CD_2Cl_2/4CDCl_3$): δ = 8.66 (s, 1 H, CCH), 7.45 (m, 5 H, Ph), 7.36 (s, 1 H, NCH), 3.86 (s, 3 H, NCH_3), 2.56 (s, 3 H, CCH_3) ppm. ^{13}C NMR ($1CD_2Cl_2/4CDCl_3$): δ = 218.9 (s, C_{carbene}), 206.3 (s, d, $^1J_{W,C}$ = 127.3 Hz, CO_{trans}), 201.5 (s, d, $^1J_{W,C}$ = 127.3 Hz, CO_{cis}), 155.6 (s, CPh), 149.6 (s, C*C*H), 145.0 (s, *C*CH_3), 138.6 (s, *i*-Ph), 133.3 (s, NCH), 130.7 (s, *o*-Ph), 129.1 (s, *m*-Ph), 128.9 (s, *p*-Ph), 43.9 (s, NCH_3), 19.7 (s, C*C*H_3) ppm. IR (ATR): $\tilde{\nu}_{\nu(CO)}$ = 2049 [s, $A_1^{(1)}$], 1962 (s, B_1), 1856 [vs, E and $A_1^{(2)}$] cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 2052 [m, $A_1^{(1)}$], 1914 [vs, E and $A_1^{(2)}$] cm^{-1}. MS (FAB): *m*/*z* (%) = 507 (5) [M]$^+$, 479 (7) [M – CO]$^+$, 423 (14) [M – 3 CO]$^+$. $C_{18}H_{13}NO_5W$ (507.14): calcd. C 42.6, H 2.6, N 2.8; found C 43.0, H 3.0, N 2.5.

Synthesis of 4: A Schlenk tube was charged with **1** (0.081 g, 0.228 mmol), [$Rh_2(\mu\text{-}Cl)_2(CO)_4$] (0.022 g, 0.057 mmol) and CH_2Cl_2 (20 mL) and connected to a bubbler. The solution was stirred for 5 h at room temperature until no CO formation was observed anymore as indicated by the bubbler. The mixture had turned from yellow to black. The mixture was filtered through Celite and the resulting filtrate was layered with diethyl ether and stored at –20 °C overnight. The precipitate was separated by filtration and the resulting filtrate dried in vacuo to afford a mixture of *cis*-**4** and *trans*-**4** (0.050 g). No separation of the isomers was possible. Crystallisation of the mixture by dissolving a small amount in CH_2Cl_2 and layering it with pentane afforded a few orange-yellow single crystals of *cis*-**4**.

***trans*-4:** Yield (according to NMR): 44%. ^1H NMR (CD_2Cl_2): δ = 8.11 (s, 1 H, CCH), 7.60 (s, 1 H, NCH), 3.94 (s, 3 H, NCH_3), 3.04 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.54 (s, 3 H, CCH_3), 1.80 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.48 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.02 (m, 3 H, $CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 211.0 (d, $^2J_{Rh,C}$ = 31.9 Hz, C_{carbene}), 188.3 (d, $^2J_{Rh,C}$ = 50.9 Hz, CO), 150.3 [s, C(*n*Bu)], 141.8 (s, C*C*H), 138.8 (s, *C*CH_3), 135.3 (s, NCH), 44.1 (s, NCH_3), 37.8 (s, C*C*H_3), 33.1 (s, $CH_2CH_2CH_2CH_3$), 23.0 (s, $CH_2CH_2CH_2CH_3$), 19.5 (s, $CH_2CH_2CH_2CH_3$), 14.1 (s, $CH_2CH_2CH_2CH_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 1905 (s) cm^{-1}.

***cis*-4:** Yield (according to NMR): 56%. ^1H NMR (CD_2Cl_2): δ = 7.89 (s, 1 H, CCH), 7.51 (s, 1 H, NCH), 3.90 (s, 3 H, NCH_3), 3.04 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.50 (s, 3 H, CCH_3), 1.71 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.48 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.02 (m, 3 H, $CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 209.2 (d, $^2J_{Rh,C}$ = 9.9 Hz, C_{carbene}), 192.2 (d, $^2J_{Rh,C}$ = 4.9 Hz, CO_{trans}), 186.1 (d, $^2J_{Rh,C}$ = 9.7 Hz, CO_{cis}), 149.7 [s, C(*n*Bu)], 141.8 (s, C*C*H), 139.6 (s, *C*CH_3), 135.3 (s, NCH), 44.4 (s, NCH_3), 38.5 (s, C*C*H_3), 33.1 (s, $CH_2CH_2CH_2CH_3$), 22.8 (s, $CH_2CH_2CH_2CH_3$), 19.5 (s, $CH_2CH_2CH_2CH_3$), 14.1 (s, $CH_2CH_2CH_2CH_3$) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 2046 (s), 1983 (s) cm^{-1}. MS (FAB): *m*/*z* (%) = 322 (7) [M – Cl]$^+$, 302 (5) [M – 2 CO]$^+$, 264 (45) [M – 2 CO – Cl]$^+$. $C_{13}H_{17}ClNO_2Rh\cdot 0.5H_2O$ (366.65): calcd. C 42.6, H 5.0, N 3.8; found C 42.3, H 5.2, N 3.6.

Synthesis of 5: The complex [AuCl(PPh_3)] was prepared in situ from [AuCl(Me_2S)] (58 mg, 0.20 mmol) and PPh_3 (52 mg, 0.20 mmol) in 10 mL of acetonitrile and the suspension was stirred at room temperature for 45 min. Separately, a solution of **2** in 20 mL of acetonitrile was prepared. Both Schlenk tubes were cooled to –45 °C. Solid NaOTf (34 mg, 0.20 mmol) was added to the solution of [AuCl(PPh_3)]. After 10 min the solution of **2** was transferred to the Schlenk tube containing the [AuCl(PPh_3)] via a Teflon cannula. Stirring continued for 4 h whereupon the cooling bath reached room temperature and the colour of the solution lightened to lemon yellow. TLC analysis (silica gel adsorbent, diethyl ether as eluent) showed that almost all chromium carbene had reacted and an apolar yellow side product, assumed to be [$Cr(CO)_5(Me_2S)$], had formed. All volatiles were removed in vacuo and the resultant solid was re-dissolved in CH_2Cl_2. A filterstick filtration and stripping of the solvent afforded a yellow residue which was extracted with toluene to remove most of the side product. Crystallisation from a CH_2Cl_2 solution layered with pentane gave colourless needles suitable for X-ray diffraction. Yield 78%, 0.12 g, m.p. 225 °C, slight onset of decomposition noticeable from 205 °C (dec.). ^1H NMR (CD_2Cl_2): δ = 8.40 (s, d, $^1J_{C,H}$ = 183.8 Hz, 1 H, CCH), 8.06 (s, d, 1 H, $^1J_{C,H}$ = 167.9 Hz, NCH), 7.81 (m, 2 H, *o*-Ph), 7.55 (m, 6 H, *o*-PPh_3), 7.44 (m, 12 H, *m,p*-Ph, *m,p*-PPh_3), 4.20 (s, d, $^1J_{CH}$ = 144.3 Hz, 3 H, NCH_3), 2.73 (s, d, $^1J_{C,H}$ = 130.5 Hz, 3 H, CCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 199.5 (br. s, C_{carbene}), 149.4 (s, CPh), 147.7 (s, C*C*H), 141.1 (s, *i*-Ph), 140.4 (s, *C*CH_3), 140.2 (s, NCH), 134.4 (d, $^2J_{P,C}$ = 14.0 Hz, *o*-PPh_3), 132.3 (d, $^4J_{P,C}$ = 1.9 Hz, *p*-PPh_3) 130.3 (d, $^1J_{P,C}$ = 62.4 Hz, *i*-PPh_3), 129.7 (d, $^3J_{P,C}$ = 11.5 Hz, *m*-PPh_3), 129.7 (s, *o*-Ph), 129.3 (s, *m*-Ph), 129.0 (s, *p*-Ph), 121.5 (q, $^1J_{C,F}$ = 321 Hz, $CF_3SO_3^-$), 45.7 (s, NCH_3), 20.1 (s, C*C*H_3) ppm. ^{31}P NMR (CD_2Cl_2): δ = 41.8 (s) ppm. MS (FAB): *m*/*z* (%) = 642 (100) [M – CF_3SO_3]$^+$, 459 (17) [M – CF_3SO_3 – PPh_3]$^+$, 380 (47) [$AuPPh_3$]$^+$. $C_{32}H_{28}AuF_3NO_3PS$ (791.58): calcd. C 48.6, H 3.6, N 1.8; found C 49.0, H 3.5, N 1.6.

Synthesis of 6: Two Schlenk tubes were charged with [AuCl(tht)] (93 mg, 0.29 mmol) and **3** (150 mg, 0.29 mmol), respectively. Both compounds were dissolved in 10 mL of CH_2Cl_2 each and the solutions were cooled to –35 °C. The [AuCl(tht)] solution was transferred to the carbene complex solution via a Teflon cannula. After the cooling bath had reached 0 °C (2 h), it was removed and the solution stirred at room temperature for another 1.5 h. Completion of the reaction was indicated by TLC (silica adsorbent, CH_2Cl_2/diethyl ether, 1:1 as mobile phase) when starting material was not detected any more and instead a spot at R_f 0.83 that can be attributed to [$W(CO)_5$(tht)] [R_f(**3**) = 0] was observed. All volatiles were removed in vacuo, the residue redissolved in 30 mL of CH_2Cl_2, filtered and concentrated to about 7 mL. Layering the solution with pentane yielded 85 mg (71%) of a cream-coloured microcrystalline solid. A crystal suitable for X-ray diffraction was obtained by recrystallising a small quantity from thf layered with pentane. Yield 71%, 0.085 g, m.p. 154 °C (dec.). ^1H NMR (CD_2Cl_2): δ = 7.99 (s, 1 H, CCH), 7.96 (s, 1 H, NCH), 7.82 (m, 2 H, *o*-Ph), 7.48 (m, 3 H, *m,p*-Ph), 3.98 (s, 3 H, NCH_3), 2.55 (s, 3 H, CCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 186.5 (s, C_{carbene}), 149.0 (s, CPh), 146.1 (s, C*C*H), 141.8 (s, *C*CH_3), 141.2 (s, NCH), 138.7 (s, *i*-Ph), 129.5 (s, *o*-Ph), 129.0 (s, *m*-Ph), 128.9 (s, *p*-Ph), 45.0 (s, NCH_3), 19.9 (s, C*C*H_3) ppm. MS (FAB): *m*/*z* (%) = 380 (100) [M – Cl]$^+$. $C_{13}H_{13}AuClN$ (415.67): calcd. C 37.6, H 3.2, N 3.4; found C 37.5, H 3.3, N 3.1.

Table 1. Crystallographic data and parameters for all crystal structures.

Compound	**3**	**4**·0.5H$_2$O	**5**	**6**	**8**
*F*ormula	$C_{18}H_{13}NO_5W$	$C_{13}H_{17}ClNO_2Rh \cdot 0.5H_2O$	$C_{32}H_{28}AuF_3NO_3PS$	$C_{13}H_{13}AuClN$	C_6H_7AuClN
M_r	507.14	366.64	791.55	415.66	325.54
Crystal habit	yellow prism	orange-yellow prism	colourless needle	colourless needle	colourless prism
Crystal size [mm]	0.10 × 0.06 × 0.06	0.10 × 0.09 × 0.06	0.51 × 0.08 × 0.07	0.28 × 0.09 × 0.03	0.06 × 0.04 × 0.02
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	12.5486(8)	19.339(3)	8.4149(4)	10.412(2)	5.7342(7)
b [Å]	10.1357(6)	11.734(2)	16.9169(9)	7.227(1)	7.3911(8)
c [Å]	14.7976(9)	13.384(2)	21.224(2)	17.365(2)	9.257(2)
α [°]	90	90	90	90	109.679(2)
β [°]	112.760(1)	93.381(3)	97.182(1)	104.892(2)	101.668(2)
γ [°]	90	90	90	90	92.292(2)
V [Å^3]	1735.6(2)	3032.0(7)	2997.6(3)	1262.8(3)	359.27(7)
Z, D_{calc} [Mg m^{-3}]	4, 1.941	8, 1.606	4, 1.754	4, 2.186	2, 3.009
μ [mm^{-1}]	6.683	1.301	5.084	11.832	20.748
F(000)	968	1480	1552	776	292
No. of reflections	18120	8775	17310	6755	3852
Unique reflections	3557	3123	6109	2567	1462
R_{int}	0.0367	0.0431	0.0258	0.0338	0.0284
R_1, wR_2[a] [$I > 2\sigma(I)$]	0.0255, 0.0551	0.0491, 0.1137	0.0235, 0.0553	0.0388, 0.0814	0.0254, 0.0530
Data, restraints, parameters	3175, 0, 228	3123, 4, 177	5499, 0, 381	2377, 6, 147	1386, 0, 83
Largest peak and hole [e Å^{-3}]	1.352, –0.544	2.850, –1.353	1.315, –0.389	3.038, –2.448	1.274, –0.784
Goodness-of-fit	1.089	1.053	1.055	1.149	1.080

[a] $w = 1/[\sigma^2(F_o)^2 + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Synthesis of 7: A 0.2 M solution of sodium naphthalenide was prepared by adding an appropriate amount of finely diced sodium metal to a solution of naphthalene in thf (100 mL in total) and stirring overnight. A suspension of [Cr(CO)$_6$] (730 mg, 3.32 mmol) in 20 mL of thf was cooled to –50 °C. The sodium naphthalenide solution (33 mL, 6.6 mmol) was added dropwise via a syringe and the naphthalenide radical anion was consumed quickly, indicated by the colour changing from green to brown. After 1 h the temperature had reached –30 °C and solid 4-chloro-1-methylpyridinium triflate (782 mg, 2.8 mmol) was added and stirring was continued for another 2 h at room temperature furnishing a black suspension. To separate any insoluble and explosive disodium ethynediolate ($Na_2C_2O_2$), the suspension was filtered under inert conditions before evaporating to dryness. The black oil obtained was purified by inert column chromatography on Florisil (12 × 5 cm) eluting with CH_2Cl_2/pentane, 1:1 (200 mL), CH_2Cl_2/pentane/diethyl ether, 3:2:1 (100 mL), CH_2Cl_2/diethyl ether, 1:1 (100 mL), and CH_2Cl_2/diethyl ether, 4:3 (100 mL). The yellow product fraction was collected and upon evaporation gave a yellow crystalline solid. Yield 11 %, 0.101 g, m.p. 143 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, CrCCH), 7.07 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, NCH), 3.93 (s, 3 H, NCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 241.2 (s, $C_{carbene}$), 226.1 (s, CO_{trans}), 220.0 (s, CO_{cis}), 144.2 (s, CrCCH), 128.5 (s, NCH), 45.4 (s, NCH_3) ppm. IR (ATR): $\tilde{\nu}_{\nu(CO)}$ = 2043 [s, $A_1^{(1)}$], 1962 (sh, B_1), 1890 [vs, E and $A_1^{(2)}$] cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}_{\nu(CO)}$ = 2044 [s, $A_1^{(1)}$], 1967 (sh, B_1), 1917 (vs, E) cm^{-1}. MS (FAB): m/z (%) = 285 (100) [M]$^+$, 257 (52) [M – CO]$^+$. $C_{11}H_7CrNO_5$ (285.17): calcd. C 46.3, H 2.5, N 4.9; found C 46.0, H 2.4, N 4.7.

Synthesis of 8: A Schlenk tube was charged with **7** (45 mg, 0.15 mmol), [AuCl(tht)] (51 mg, 0.16 mmol) and 5 mL of CH_2Cl_2 was added. Partial decomposition of [AuCl(tht)] was immediately observed by the characteristic purple gold precipitate, the suspension was stirred for 2 h at room temperature. Filtration, evaporation of all volatiles in vacuo and extraction of side products with diethyl ether (ca. 20 mL) afforded a colourless microcrystalline solid. Crystals just large enough for X-ray diffraction were obtained from a thf solution layered with pentane. Yield 27 %, 0.014 g, m.p. 140 °C (dec.). ^{1}H NMR (CD_2Cl_2): δ = 8.32 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, AuCCH), 7.92 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, NCH), 4.30 (s, d, $^1J_{C,H}$ = 144 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 185.3 (s, $C_{carbene}$), 140.1 (s, AuCCH), 139.7 (s, NCH), 47.2 (s, NCH_3) ppm. MS (FAB): m/z (%) = 615 (11) [2 M – Cl]$^+$, 290 (100) [M – Cl]$^+$. C_6H_7AuClN (325.55): calcd. C 22.1, H 2.2, N 4.3; found C 22.0, H 2.3, N 4.2.

Crystallography: Data associated with the crystal structures are summarised in Table 1. Intensity data were collected at T = 100 K with a Bruker SMART Apex diffractometer[37] with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensities were measured using the ω-scan mode and were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 software package within the X-SEED environment.[38] All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions if not noted otherwise. Thermal ellipsoids in all figures are at the 50 % probability level and hydrogen atoms have been omitted for clarity except in Figure 5. In **4**·0.5H$_2$O the hydrogen of the water molecule was restrained to an O–H bond length of 0.99 Å and a H–H distance of 1.57 Å; U_{iso}(H) was set 1.2 times U_{eq}(O). The three terminal carbon atoms in the butyl chain were restrained to show the same displacement parameters. In the structure of **6**, C4 was restrained to approximate isotropic behaviour.

CCDC-710168 (for **3**), -710169 (for **4**), -710170 (for **5**), -710171 (for **6**), -710172 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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