Gold(III) Alkene Complexes

DOI: 10.1002/anie.201208356

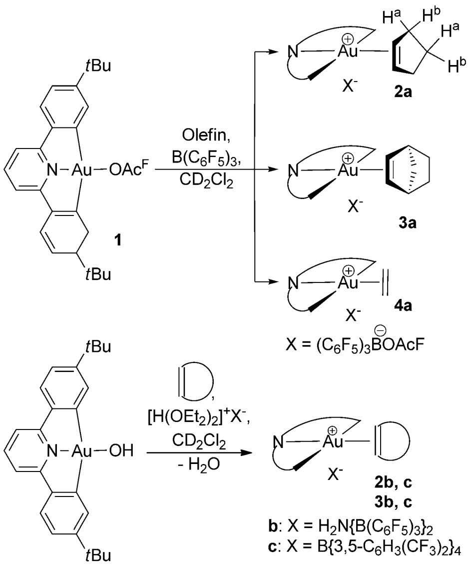
Gold(III) Olefin Complexes**

*Nicky Savjani, Dragoş-Adrian Roşca, Mark Schormann, and Manfred Bochmann**

Zeise's salt, K[$PtCl_3(C_2H_4)$], was first reported in 1827 and is generally regarded as the prototypical transition-metal olefin complex.[1] It displays the square-planar structure[2] typical of a heavy transition metal with the d^8 electron configuration, a structural feature shared with innumerable d^8 noble-metal olefin complexes of the cobalt and nickel triads. It is surprising then that analogous olefin complexes of its isoelectronic and isostructural neighbor in the periodic table, gold(III), are not known. By contrast, alkene and alkyne complexes of gold(I) were first isolated in the 1960s and 70s, mainly by the pioneering work of Hüttel.[3] This area has experienced a dramatic resurgence in recent years, an interest fuelled by the growing importance of gold complexes as catalysts where formation of gold olefin or acetylene complexes is frequently postulated as the first step of a catalytic cycle.[4] Gold(III) catalysts or catalyst precursors are employed in a multitude of reactions including inter- and intramolecular additions of nucleophiles to C–C double and triple bonds, C–H bond activations, C–C bond formations, hydrogenations and the like, most commonly in the form of gold(III) halide compounds.[5–9] These reactions can only be rationalized by assuming the coordination of an alkene or alkyne to the metal center as the first step of the catalytic cycle. On the other hand, earlier efforts to generate gold(III) olefin complexes were unsuccessful, and reactions of typical gold(III) starting materials, such as $AuCl_3$, $AuBr_3$, $HAuCl_4$ or $NaAuCl_4$, with olefins or dienes invariably led to reduction to gold(I) or gold metal,[3] which is not surprising perhaps in view of the strongly positive standard redox potentials for Au^{3+} ions ($Au^{3+}/Au^+ = 1.36$ V; $Au^{3+}/Au^0 = 1.52$ V).[10] We decided to reinvestigate the possible synthesis of gold congeners of Pt^{II} π-complexes and report herein the synthesis and some reactions of gold(III) alkene complexes.

Initial experiments seemed to confirm the earlier reports. For example, attempts to displace the ether ligands in the known[11] gold(III) cation $[(C_6F_5)_2Au(OEt_2)_2]^+$ with norbornene or 1,5-cyclooctadiene showed no reaction, while chloride abstraction from $[(C_6F_5)_2AuCl_2]^-$ with $AgSbF_6$ in the presence of norbornene gave mainly $[Au(norbornene)_3]^+$ alongside perfluorobiphenyl as the product of reductive elimination.

However, employing gold(III) complexes based on the reduction-resistant (C^N^C)* pincer ligand, where (C^N^C)* = 2,6-bis(4-tBuC_6H_3)$_2$pyridine dianion, were more successful. Thus adding cyclopentene to a solution of the gold trifluoroacetato complex **1**[12] in dichloromethane at −40 °C in the presence of $B(C_6F_5)_3$ gave the cyclopentene complex **2a** (Scheme 1). The norbornene and ethylene complexes **3a** and **4a**, respectively, were obtained in analogous manner. An alternative route to these complexes starts with the gold(III) hydroxide (C^N^C)*AuOH, which reacts with $[H(OEt_2)_2]^+X^-$ ($X = H_2N[B(C_6F_5)_3]_2$ or $B[3,5\text{-}C_6H_3(CF_3)_2]_4$) in the presence of olefins under the same conditions. In this case, a few granules of 4 Å molecular sieves were added to remove the produced water. The yields were essentially quantitative in all cases.



Scheme 1. Synthetic routes to gold(III) alkene complexes.

In solution, the cyclopentene and ethylene complexes are stable up to about 0 and −20 °C, respectively, when changes in the pincer ligand pattern are becoming apparent. The norbornene complex is stable at 20 °C. Removal of volatiles below −30 °C (**2a**, **4a**) or below 0 °C (**3a**) affords the complexes as yellow powders which are stable under nitrogen; **3c** was isolated as yellow needles. Once isolated, these complexes are stable in the solid state for hours at room temperature and in air with minimal degradation. Up to now, crystals suitable for X-ray diffraction could unfortunately not be obtained, even though various different counteranions and crystallization methods were tried.

---

[*] Dr. N. Savjani, D.-A. Roşca, Dr. M. Schormann,
Prof. Dr. M. Bochmann
Wolfson Materials and Catalysis Centre, School of Chemistry,
University of East Anglia
Norwich, NR4 7TJ (UK)
E-mail: m.bochmann@uea.ac.uk

[**] This work was supported by the Leverhulme Trust and Johnson Matthey plc. N.S. and D.A.R. thank the University of East Anglia for studentships.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208356.

Coordination of cyclopentene in **2a** was indicated by a downfield shift of the olefinic proton signal from $\delta = 5.74$ to 6.3 ppm, as well as by the loss of equivalence of the methylene protons which in the complex appear as four multiplets.[13] By contrast, the norbornene complexation in **3a** is associated with a small upfield shift of the olefinic resonances, from $\delta = 6.02$ to 5.8.

It is well-established that norbornene has a greater ring-strain than cyclopentene, a factor that strengthens alkene coordination and back-bonding.[14] The small chemical shift change of the alkene signals in **3a** can be understood as the consequence of two opposing trends: π-donation to a cationic metal center and back-donation, which almost cancel one another out. Clear and unequivocal indication for norbornene coordination is however provided by the bridgehead protons, which display a strong shift to lower frequency, from $\delta = 2.84$ to 3.49, as well as by the protons in the 5- and 6-positions of the norbornene framework, which are also downfield shifted from $\delta = 1.62$ to 1.97. These signals remain invariant from -40 to $+20\,^{\circ}$C.[15] Neither **2a** nor **3a** show evidence for alkene rotation or ligand exchange processes between free and coordinated alkenes. For all of the alkene complexes, the addition of SMe_2 to the NMR samples produced $[(C\text{^}N\text{^}C)^{*}Au(SMe_2)]^+$ together with the signals of the free olefins.

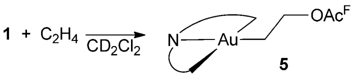
The coordination of ethylene in **4a** is indicated by a ^{1}H chemical shift change from $\delta = 5.38$ in free C_2H_4 to $\delta = 6.29$ at $-40\,^{\circ}$C. In the presence of excess ethylene, the ^{1}H NMR signals broaden on warming from -70 to $-10\,^{\circ}$C, which is indicative of ligand exchange, while in the absence of excess ethylene a sharp signal for coordinated C_2H_4 is observed over this temperature range. The formation of an ethylene complex was confirmed using $^{13}C_2H_4$; the $^{13}C\{^1H\}$ NMR resonance of coordinated ethylene was observed at $\delta = 108.9$, up from $\delta = 122.8$ for the free alkene, while the C–H coupling constant increased on coordination from 156 to 166 Hz. Similar J_{CH} values have been found for gold(I) ethylene complexes, although in those cases the changes in the ^{13}C NMR chemical shifts are larger, of the order of more than 60 ppm.[16,17] Table 1 summarizes pertinent NMR spectroscopic parameters of Au^{I}, Au^{III}, and Pt^{II} ethylene complexes for comparison. The data suggest comparable π-donation and back-bonding in gold and platinum complexes.

Table 1: Comparison of NMR data of selected gold(I), platinum(II), and gold(III) ethylene and cyclopentene complexes.[a]

Compound	δ^1H	$\Delta\delta$ (H)	δ^{13}C	$\Delta\delta$ (C)	J_{CH}[b]	Ref.
C_2H_4	5.38		122.8		156	
$[Au(C_2H_4)_3]SbF_6$	4.94	−0.44	92.7			[17]
$HB(pz^{CF3})_3Au(C_2H_4)$[c,d]	3.81	−1.6	63.7	−59.8	165	[16]
$[(2\text{-}R\text{-}bipy)Au(C_2H_4)]PF_6$[e]	3.09	−2.3	61.6	−55.2		[18]
$K[PtCl_3(C_2H_4)]$[f]	4.83	−0.55	67.1	−55.7		[19,22]
$(py)PtCl_2(C_2H_4)$[g]	4.93	−0.45				[20]
$[MePt(PMe_2Ph)_2(C_2H_4)]PF_6$[g]	4.12	−1.26	84.8	−38.4		[21,22]
4a	6.29	0.91	108.9	−13.9	166	This work
$(py)PtCl_2$(cyclopentene)[g]	6.23	0.49				[20]
2a	6.30	0.56				This work

[a] In CD_2Cl_2 unless indicated otherwise. [b] In Hz. [c] $pz^{CF3} = 3,5\text{-}(CF_3)_2C_3N_2$. [d] In $CDCl_3$. [e] R = 2,6-$Me_2C_6H_3$. [f] In 1 м methanolic HCl. The chemical shift of free C_2H_4 in this solvent is $\delta = 5.37$. [g] *Trans* isomer, py = pyridine.

A different course of reaction was observed when **1** was allowed to react with ethylene at room temperature in the absence of $B(C_6F_5)_3$ over the course of 14–72 h. Quantitative insertion of ethylene into the Au–OAc^F bond was observed to give **5** [Eq. (1)]. Attempts at crystallization resulted in a small crop of crystals of **5**·3 AgOAc^F that proved suitable for X-ray diffraction studies (Figure 1). Closer inspection showed that this particular sample of **1** contained about 6 mol % AgOAc^F remaining from its preparation (by ^{19}F NMR), which explained the low yield of crystalline material. The geometric parameters of **5** are as expected, but the gold complex is associated with a polymeric ribbon of silver trifluoroacetate (Figure 2). This ribbon is similar to the structure[23] of $[AgOAc^F]_n$, with subtle deviations (see the Supporting Information).



(1)

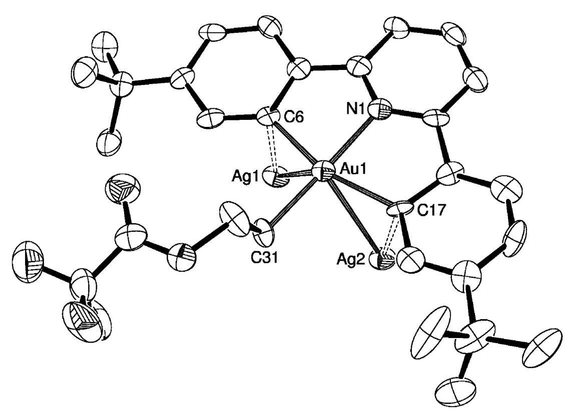


Figure 1. Partial view of **5**·3 AgOAc^F showing the Au^{III}–Ag interactions. Ellipsoids are set at 50% probability; hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Au1–N1 2.048(10), Au1–C31 2.055(11), Au1–C6 2.063(10), Au1–C17 2.080(10), Au1–Ag2 2.9367(10), Au1–Ag1 3.0789(10); N1-Au1-C31 178.4(4), C6-Au1-C17 162.0(4), N1-Au1-C6 80.9(4), C31-Au1-C6 97.8(5), N1-Au1-C17 81.1(4), C31-Au1-C17 100.2(4), C6-Au1-Ag2 122.6(3), C17-Au1-Ag2 58.0(3), C6-Au1-Ag1 51.3(3), C17-Au1-Ag1 128.7(3), Ag2-Au1-Ag1 72.07(3).

There is much interest in "metallophilic" interactions between electron-rich heavy metals. These form a common feature for closed-shell d^{10} elements and are a prominent feature of gold(I) chemistry, but evidence is scant for the smaller and less electron-rich gold(III),[24] and indeed we have been unable to find structurally characterized precedents for Au^{III}–Ag interactions in the CCDC crystallographic database. In **5**·3 AgOAc^F, each Au

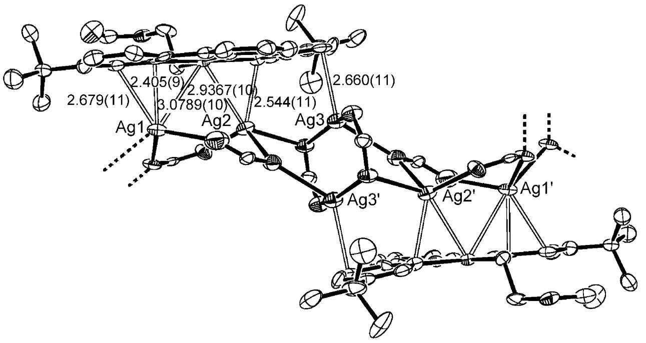


Figure 2. Side view of **5**·3 AgOAc^F, showing the interactions of **5** with the polymeric AgOAc^F ribbon through Ag–Au and Ag–arene π-interactions.

atom has two close Au···Ag contacts of 2.9367(10) and 3.0789(10) Å, which could be interpreted as Au^{III}···Ag metallophilic bonding. These Au···Ag distances are only slightly longer than those found in a number of Au^{I}···Ag clusters containing silver trifluoroacetate.[25] The association of **5** with the silver ions is further reinforced by η^1- and η^2-interactions of Ag$^+$ ions with the π-electron density of the aromatic C^N^C* ligand system. The Ag–C distances range from 2.405(9) to 2.679(11) Å and are closely comparable to the metal π-ligand bond lengths found in silver–benzene complexes.[26] The structure of **5**·3 AgOAc^F may be regarded as a model for the adsorption of a planar aromatic system to a polar solid support. The relative contributions of π-donation to Ag$^+$ and metallophilic Au^{III}···Ag$^+$ interactions to this molecular association have yet to be determined; at this stage we feel that dipolar Ag$^+$···π interactions are likely to be important factors.

In an attempt to obtain crystallographic confirmation for the norbornene complex, a different synthetic approach was tried, with the reaction of (C^N^C)*AuCl with $AgSbF_6$ in the presence of norbornene. The resulting product was identified by X-ray diffraction as the norbornolyl complex **6**·SbF_6 (Figure 3). Evidently this is the product of the reaction of **3a** with adventitious water, which has led to nucleophilic attack by OH^- on coordinated norbornene, while the gold–phenyl bond was cleaved by H^+. The structure of **6**·SbF_6 suggests that in **3a** the norbornene is bonded by its *exo*-face, as is usually observed. Cleavage of the tridentate pincer in (C^N^C)*Au complexes has been seen before, but only by strong acids.[27] Interestingly, while the hydration of alkynes by gold catalysts has been widely studied, alkene hydration has received scant attention. Similarly, the reaction of (C^N^C)*AuOH with $[H(OEt_2)_2][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ in the presence of norbornene and water generated **6**·BAr^F_4 in high yield. The addition of methanol to coordinated norbornene proceeds in analogous fashion and affords the norbornyl methyl ether complex **7** (Scheme 2).

In principle, this alkene hydration reaction should be capable of proceeding under catalytic conditions, provided the gold–alkyl bond is efficiently protolyzed. In practice this does not prove to be the case. It was shown recently that the rates of protolysis of Au^{I}–C bonds strongly depend on the donor strength of the ligands in the *trans* position,[28] and we suspect that in **6**$^+$, the pyridine-N donor is not strong enough to facilitate Au–C bond cleavage. This was confirmed by the failure of this bond to react with excess HOAc^F or $[H(OEt_2)_2][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$.

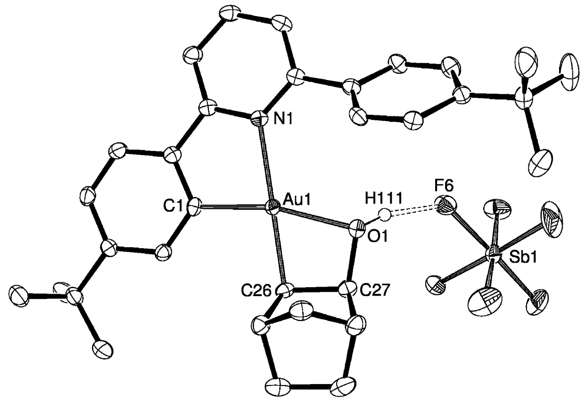
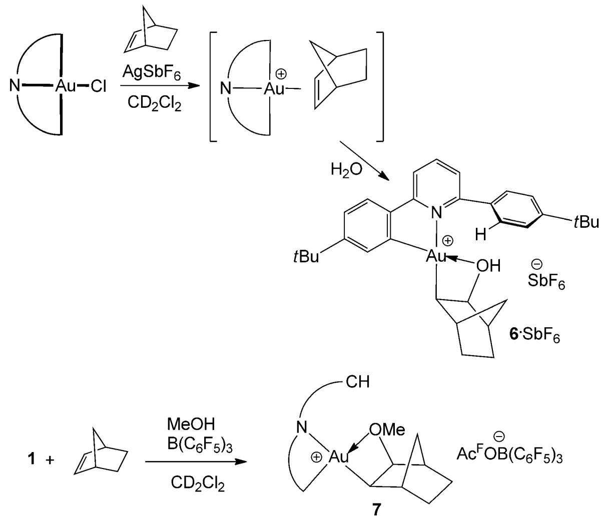


Figure 3. Molecular structure of **6**·SbF_6. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Au–C1 1.995(3), Au–C26 2.049(3), Au–O1 2.159(2), Au–N1 2.180(2); C1-Au-C26 98.23(11), C1-Au-O1 166.31(10), C1-Au-N1 81.20(10), N1-Au-C26 179.26(10), O1-Au-N1 112.42(8).



Scheme 2. Nucleophilic attack on gold(III) norbornene complexes.

In summary, we have shown, some 185 years after the well-known ethylene complex of platinum(II), that olefin complexes of its isoelectronic neighbor in the periodic table, gold(III), could be prepared and isolated. An important stabilizing factor is a ligand framework that disfavors reductive elimination. The complexes are thermally less stable than platinum analogues and, being cationic, are highly susceptible to nucleophilic attack, including by weak nucleophiles such as trifluoroacetate. The resulting gold(III) alkyls are stable towards protonolysis. Structural studies have also provided a rare example of a structurally characterized mixed-metal complex suggestive of metallophilic Au^{III}···Ag interactions.

Received: October 17, 2012
Revised: November 8, 2012

Keywords: aurophilic bonds · coordination chemistry · ethylene · gold · homogeneous catalysis

[1] W. C. Zeise, *Poggendorfs Ann. Phys.* **1827**, *9*, 632; W. C. Zeise, *Poggendorfs Ann. Phys.* **1831**, *21*, 497.

[2] J. A. Wunderlich, D. P. Mellor, *Acta Crystallogr.* **1954**, *7*, 130; G. B. Bokii, G. A. Kukina, *Zh. Strukt. Khim.* **1965**, *5*, 706; J. A. J. Jarvis, B. T. Kilbourn, P. G. Owsten, *Acta Crystallogr. Sect. B* **1971**, *27*, 366–372; M. Black, R. H. B. Mais, P. G. Owston, *Acta Crystallogr. Sect. A* **1969**, *25*, 1753–1759; R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews, R. Bau, *Inorg. Chem.* **1975**, *14*, 2653–2657.

[3] Review: H. Schmidbaur, A. Schier, *Organometallics* **2010**, *29*, 2.

[4] Selected reviews: a) A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51–65; b) A. S. K. Hashmi, *Angew. Chem.* **2005**, *117*, 7150–7154; *Angew. Chem. Int. Ed.* **2005**, *44*, 6990–6993; c) A. S. K. Hashmi, R. Salathé, T. M. Frost, L. Schwarz, J.-H. Choi, *Appl. Catal. A* **2005**, *291*, 238–246; d) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; e) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; f) X. Sun, W. Sun, R. Fan, J. Wu, *Adv. Synth. Catal.* **2007**, *349*, 2151–2155; g) Z. Li, C. Brower, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; h) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; i) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; j) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; k) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782; l) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; m) N. D. Shapiro, F. D. Toste, *Synlett* **2010**, 675–691; n) H. Schmidbaur, A. Schier, *Z. Naturforsch. B* **2011**, *66*, 329–350; o) M. Rudolph, A. S. K. Hashmi, *Chem. Commun.* **2011**, *47*, 6536–6544; p) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448–2462; q) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358–1367; r) A. Leyva-Pérez, A. Corma, *Angew. Chem.* **2012**, *124*, 636–658; *Angew. Chem. Int. Ed.* **2012**, *51*, 614–635; s) L. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129–3139.

[5] Review: H. Schmidbaur, A. Schier, *Arabian J. Sci. Eng.* **2012**, *37*, 1187–1225.

[6] Hydrogenations with Au^{III}: a) A. Comas-Vives, C. Gonzalez-Arellano, A. Corma, M. Iglesias, F. Sanchez, G. Ujaque, *J. Am. Chem. Soc.* **2006**, *128*, 4756–4765; b) A. Corma, P. Concepción, P. Serna, *Angew. Chem.* **2007**, *119*, 7404–7407; *Angew. Chem. Int. Ed.* **2007**, *46*, 7266–7269; c) A. Corma, P. Serna, H. García, *J. Am. Chem. Soc.* **2007**, *129*, 6358–6359; d) M. Boronat, P. Concepción, A. Corma, S. González, F. Illas, P. Serna, *J. Am. Chem. Soc.* **2007**, *129*, 16230–16237; e) X. Zhang, H. Shi, B. Q. Xu, *Angew. Chem.* **2005**, *117*, 7294–7297; *Angew. Chem. Int. Ed.* **2005**, *44*, 7132–7135.

[7] Hydrosilylation: a) D. Lantos, M. Contel, S. Sanz, A. Bodor, I. T. Horvath, *J. Organomet. Chem.* **2007**, *692*, 1799–1805; b) A. Corma, C. González-Arellano, M. Iglesias, F. Sánchez, *Angew. Chem.* **2007**, *119*, 7966–7968; *Angew. Chem. Int. Ed.* **2007**, *46*, 7820–7822.

[8] Isomerization: a) C. M. Ting, Y. L. Hsu, R. S. Liu, *Chem. Commun.* **2012**, *48*, 6577–6579; b) M. Muuronen, J. E. Perea-Buceta, M. Nieger, M. Patzschke, J. Helaja, *Organometallics* **2012**, *31*, 4320–4330.

[9] C–H activation: a) A. S. K. Hashmi, S. Schäfer, M. Wölfle, C. D. Gil, P. Fischer, A. Laguna, M. C. Blanco, M. C. Gimeno, *Angew. Chem.* **2007**, *119*, 6297–6300; *Angew. Chem. Int. Ed.* **2007**, *46*, 6184–6187; b) Z. Li, D. A. Capretto, R. O. Rahaman, C. He, *J. Am. Chem. Soc.* **2007**, *129*, 12058–12059; c) J. Xie, H. Li, J. Zhou, Y. Cheng, C. Zhu, *Angew. Chem.* **2012**, *124*, 1278–1281; *Angew. Chem. Int. Ed.* **2012**, *51*, 1252–1255.

[10] A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, **1985**.

[11] R. Usón, A. Laguna, M. L. Arese, *Synth. React. Inorg. Metal-Org. Chem.* **1984**, *14*, 557–567.

[12] D.-A. Roşca, D. A. Smith, M. Bochmann, *Chem. Commun.* **2012**, *48*, 7247–7249; D.-A. Roşca, D. A. Smith, D. L. Hughes, M. Bochmann, *Angew. Chem.* **2012**, *124*, 10795–10798; *Angew. Chem. Int. Ed.* **2012**, *51*, 10643–10646.

[13] The ^{1}H NMR pattern of the coordinated cyclopentene resembles that observed for [W(CO)$_4$(cyclopentene)$_2$]: M. Jaroszewski, T. Szymánska-Buzar, M. Wilgocki, J. J. Ziółkowski, *J. Organomet. Chem.* **1996**, *509*, 19–28.

[14] C. A. Tolman, *J. Am. Chem. Soc.* **1974**, *96*, 2780–2789.

[15] The convergence seen for the olefinic ^{1}H NMR signals of free and bound norbornene on warming from −40 to +20°C is due to a temperature effect on the chemical shifts, which leads to accidental overlap, as confirmed by the lack of change or broadening of the other norbornene signals over this temperature range (see the Supporting Information).

[16] a) H. V. R. Dias, J. Wu, *Angew. Chem.* **2007**, *119*, 7960–7962; *Angew. Chem. Int. Ed.* **2007**, *46*, 7814–7816; b) J. A. Flores, H. V. R. Dias, *Inorg. Chem.* **2008**, *47*, 4448–4450; c) H. V. R. Dias, J. Wu, *Organometallics* **2012**, *31*, 1511–1517.

[17] H. V. R. Dias, M. Fianchini, T. R. Cundari, C. F. Campana, *Angew. Chem.* **2008**, *120*, 566–569; *Angew. Chem. Int. Ed.* **2008**, *47*, 556–559.

[18] M. A. Cinellu, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, M. Arca, *Dalton Trans.* **2006**, 5703–5716.

[19] D. B. Powell, N. Sheppard, *J. Chem. Soc.* **1960**, 2519–2521; R. Cramer, *Inorg. Chem.* **1965**, *4*, 445–447.

[20] W. Partenheimer, *J. Am. Chem. Soc.* **1976**, *98*, 2779–2784.

[21] M. H. Chisholm, H. C. Clark, *Inorg. Chem.* **1973**, *12*, 991–998.

[22] M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, *J. Am. Chem. Soc.* **1972**, *94*, 5087–5089.

[23] E. V. Karpova, A. I. Boltalin, Y. M. Korenev, S. I. Troyanov, *Russ. J. Coord. Chem.* **1999**, *25*, 65–68.

[24] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951, H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412.

[25] See for example: E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Perez, R. C. Puelles, J. C. Saenz, *Dalton Trans.* **2005**, 1162–1164; E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. C. Puelles, *Organometallics* **2007**, *26*, 5931–5939; E. J. Fernández, C. Hardacre, A. Laguna, M. C. Lagunas, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, R. C. Puelles, E. Sánchez-Forcada, *Chem. Eur. J.* **2009**, *15*, 6222–6233; T. Lasanta, M. E. Olmos, A. Laguna, J. M. López-de-Luzuriaga, P. Naumov, *J. Am. Chem. Soc.* **2011**, *133*, 16358–16361.

[26] E. A. H. Griffith, E. L. Amma, *J. Am. Chem. Soc.* **1974**, *96*, 743; K. Shelly, D. C. Finster, Y. J. Lee, R. Scheidt, C. A. Reed, *J. Am. Chem. Soc.* **1985**, *107*, 5955; K. Ogawa, T. Kitagawa, S. Ishida, K. Komatsu, *Organometallics* **2005**, *24*, 4842.

[27] D. A. Smith, D.-A. Roşca, M. Bochmann, *Organometallics* **2012**, *31*, 5998–6000.

[28] W. Wang, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 5697–5705.