The First Acetimine Gold(I) and Gold(III) Complexes and the First Acetonine Complexes**

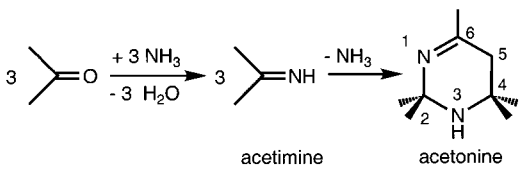
José Vicente,*[a] M. Teresa Chicote,*[a] Rita Guerrero,[a] Isabel M. Saura-Llamas,[a] Peter G. Jones,*[b] and M. Carmen Ramírez de Arellano*[a]

Abstract: Ketimino(phosphino)gold(I) complexes of the type [Au{NR=C(Me)R′}L]X (X = ClO_4, R = H, L = PPh_3, R′ = Me (**1a**), Et (**2a**); L = PAr_3 (Ar = C_6H_4OMe-4), R′ = Me (**1b**), Et (**2b**); L = PPh_3, R = R′ = Me (**3**); X = CF_3SO_3 (OTf), L = PPh_3, R = R′ = Me (**3′**); R = Ar, R′ = Me (**4**)) have been prepared from [Au(acac)L] (acac = acetyl acetonate) and ammonium salts $[RNH_3]X$ dissolved in the appropriate ketone MeC(O)R′. Complexes $[Au(NH{=}CMe_2)_2]X$ (X = ClO_4 (**6**), OTf (**6′**)) were obtained from solutions of $[Au(NH_3)_2]X$ in acetone. The reaction of **6** with PPN[$AuCl_2$] or with $PhICl_2$ gave [AuCl(NH=CMe_2)] (**7**) or $[AuCl_2(NH{=}CMe_2)_2]ClO_4$ (**8**), respectively. Complex **7** was oxidized with $PhICl_2$ to give $[AuCl_3(NH{=}CMe_2)]$ (**9**). The reaction of [AuCl(tht)] (tht = tetrahydrothiophene), $NaClO_4$, and ammonia in acetone gave [Au(acetonine)$_2$]-ClO_4 (**10**) (acetonine = 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) which reacted with PPh_3 or with PPN[$AuCl_2$] to give [Au(PPh_3)(acetonine)]ClO_4 (**11**) or [AuCl(acetonine)] (**12**), respectively. Complex **11** reacts with $[Au(PPh_3)(Me_2CO)]ClO_4$ to give $[(AuPPh_3)_2(\mu\text{-acetonine})](ClO_4)_2$ (**13**). The reaction of $AgClO_4$ with acetonine gave [Ag(acetonine)($OClO_3$)] (**14**). The crystal structures of [Au(NH_2Ar)(PPh_3)]OTf (**5**), **6′** and **10** have been determined.

Keywords: acetimine · acetonine · gold · N ligands · structure elucidation

Introduction

Imines are important synthetic intermediates since they perform a significant role in functional group transformations, carbon–carbon bond formation, and ring construction.[2] N-substituted imines are generally stable, can be obtained by several straightforward methods and serve as ligands in many metal complexes.[3] Unlike N-substituted imines, the unsubstituted NH-aldimines, HN=CHR, or NH-ketimines, HN=CRR′, are, with the exception of diarylketimines, unstable compounds that need to be trapped with various reagents.[2] In particular, HN=CMe_2 (acetimine) can be prepared from acetone and ammonia, but requires an ammonium chloride-catalyzed reaction at 50 bar and 120 °C[4] or the use of zeolite HZSM-5 over 250 °C.[5] Although it is stable at 0 °C for short periods of time it decomposes on storage to give 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine (acetonine; see Scheme 1).[6] The difficulties associated with the preparation and handling of acetimine could account for the scarcity of complexes with this ligand; in particular, there are none with gold.[7–17] The only gold(I) complexes with NH-ketimines contain the stable ligands diphenylmethanimine[18] and tetramethylguanidine and are



Scheme 1. The formation of acetimine from acetone and ammonia. Conditions: either a) NH_4Cl catalyst, 50 bar, 120 °C; or b) zeolite HZSM-5 catalyst, 250 °C. Acetimine is stable for short periods at 0 °C, but eventually decomposes to give acetonine.

[a] Prof. J. Vicente, Prof. M. T. Chicote, Dr. M. C. Ramírez de Arellano,[+] Dr. R. Guerrero, Dr. I. M. Saura-Llamas
Grupo de Química Organometálica,
Departamento de Química Inorgánica
Facultad de Química, Universidad de Murcia
Apartado 4021, 30071 Murcia (Spain)
WWW: http://www.scc.um.es/gi/gqo/
E-mail: jvs@um.es, mch@um.es, ims@um.es, mcra@uv.es

[b] Prof. P. G. Jones[++]
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig Postfach 3329
38023 Braunschweig (Germany)
E-mail: jones@xray36.anchem.nat.tu-bs.de

[+] Corresponding author regarding the X-ray diffraction study of complex **10**. Present address: Departamento de Química Orgánica, Facultad de Química, Universidad de Valencia, 46071 Valencia (Spain)

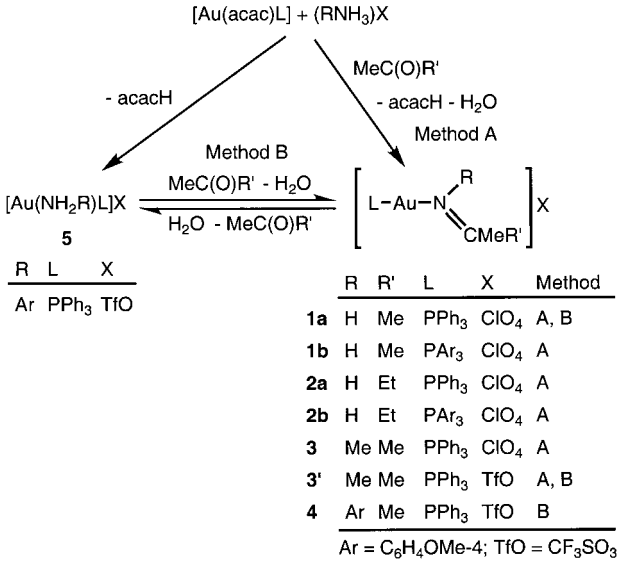
[++] Corresponding author regarding the X-ray diffraction studies of complexes **5** and **6′**

[**] Gold Complexes with N Donor Ligands, Part 4; Part 3: See ref. [1].

0947-6539/01/0703-0638 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 3

prepared by using replacement reactions.[19] There exists only one gold(I) complex with an NH-aldimine, [AuCl(NH=CH*n*Pr)], formed in the reaction between $[AuCl_4]^-$ and $nBuNH_2$.[20] The only reported gold(III) complexes with imines contain cyclic ketimines (pyridines, pyrazolato, porphyrins, etc.).[21] Here we report a family of gold(I) and gold(III) complexes with noncyclic ketimines, including acetimine, using two different synthetic methods. We have preliminarily reported the synthesis and the crystal structure of $[Au(NH{=}CMe_2)_2]OTf$.[22]

Acetonine (Scheme 1) was first characterized by Bradbury et al.[23] in 1947 based on its molecular refraction and its reduction and hydrolysis products, although it could have been first prepared by Städeler[24] more than a century ago. It has been reported to form among the decomposition products of acetimine ($NH{=}CMe_2$)[6] but it is best obtained from the reaction of acetone with ammonia, and many attempts are currently reported, most of them patents, to improve its synthesis. Thermal[25] or photochemical[26] activation as well as a wide variety of catalysts including Mg/Al complexes,[27] Fe carboxylates,[28] halo complexes of B, Al, Si, P, As, Ti, Pd, Pt,[29] zeolites,[30] NH_4Cl,[31] or *p*-nitro-calix[4]arene[32] have been used to that purpose. Acetonine finds its main use in its reaction with acetone to give triacetonamine (2,2,6,6-tetramethyl-4-oxopiperidine). This reaction has been also the subject of many patents[27, 29, 33–35] and may be a major industrial method for the synthesis of this compound, which is an attractive intermediate for the synthesis of nitroxides, oxoammonium salts,[36] pharmaceutical products, pesticides and photostabilizers for polymers. After so much work devoted to this subject and the interest in this compound we were surprised to find that, as far as we can establish, no X-ray study had been reported on acetonine or any other 2,2,4,4,6-substituted tetrahydropyrimidine and not a single acetonine complex of any element has been described. Here we report a family of acetonine complexes of gold(I) and one of silver(I). The synthesis and the crystal structure of $[Au(acetonine)_2]ClO_4$[1] was the subject of a preliminary communication.



R	L	X
Ar	PPh_3	TfO

	R	R'	L	X	Method
1a	H	Me	PPh_3	ClO_4	A, B
1b	H	Me	PAr_3	ClO_4	A
2a	H	Et	PPh_3	ClO_4	A
2b	H	Et	PAr_3	ClO_4	A
3	Me	Me	PPh_3	ClO_4	A
3'	Me	Me	PPh_3	TfO	A, B
4	Ar	Me	PPh_3	TfO	B

Ar = C_6H_4OMe-4; TfO = CF_3SO_3

Scheme 2. The synthesis of ketimino(phosphino)gold(I) complexes (**1**–**4**) from equimolar amounts of [Au(acac)L] and $[RNH_3]X$ dissolved in the appropiate ketone MeC(O)R′.

Results and Discussion

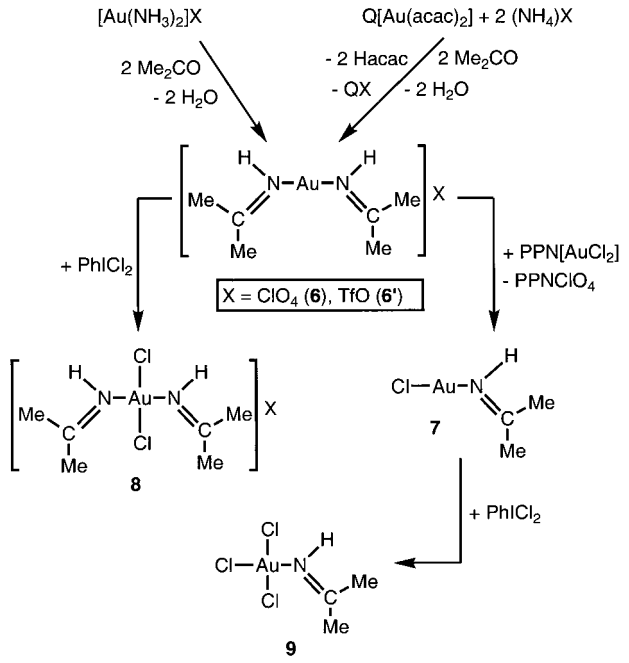
Synthesis of imino complexes of gold(I) and (III): Ketimino(phosphino)gold(I) complexes of the type [Au{N(R)=C(Me)R′}L]X (**1**–**3′**; Scheme 2, method A) were synthesized by reacting equimolar amounts of [Au(acac)L] (acac = acetyl acetonate)[37] and ammonium salts, $[RNH_3]X$, dissolved in the appropriate ketone MeC(O)R′. We have previously reported[38, 39] the synthesis of amino(phosphino)gold(I) complexes $[Au(NH_nR_{3-n})L]^+$ from the same reagents ([Au(acac)L] and $[R_nNH_{4-n}]^+$, L = PPh_3, PAr_3) that we have now used in the syntheses of **1**–**3**. In that report we stated that, whereas complexes containing secondary or tertiary amines as ligands could be prepared in acetone, in the synthesis of those with primary amines, Et_2O must be used instead of acetone. We reasoned that the insolubility of $[Au(NH_2R)L]^+$ in Et_2O prevented its contamination with dinuclear complexes $[(AuL)_2(\mu\text{-}NHR)]^+$, formed from the reaction between [Au(acac)L] and $[Au(NH_2R)L]^+$. According to the present results, the above facts could be interpretated differently as a consequence of formation of ketimine complexes $[Au\{N(R){=}CMe_2\}L]^+$. In fact, complexes **1a** and **3′** can also be obtained by stirring solutions of the corresponding $[Au(NH_2R)L]^+$ complexes in acetone (Scheme 2, method B). The complex $[Au\{N(Ar){=}CMe_2\}PPh_3]OTf$ (**4**) has been prepared by using method B. Therefore, reactions giving complexes **1**–**3** by method A occur through the intermediacy of amino complexes $[Au(NH_2R)L]^+$. However, the reverse reaction of the condensation process leading to complexes **1**–**3** (hydrolysis) is important in some cases. Thus, the ^1H NMR spectrum of an analytically pure sample of complex **2a** shows traces of the hydrolysis product $[Au(NH_3)(PPh_3)]ClO_4$. Similarly, complex **4** partly hydrolyzes upon standing in solution to give $[Au(NH_2Ar)(PPh_3)]OTf$ (**5**) which accounts for both the low yield of pure **4** and the growth of single crystals of **5** (see Figure 1) from solutions of **4**.

In several reactions meant to establish the generality of this method for the synthesis of imino(phosphino)gold(I) complexes we have found that 1) complexes $[Au(n\text{-}NH_2C_6H_4NO_2)(PPh_3)]X$ ($n = o$, p) and $[\{Au(PPh_3)\}_2\{\mu\text{-}NH_2(CH_2)_2NH_2\}]X_2$ (X = OTf) do not react with acetone, 2) $[Au(NH_3)(PPh_3)]ClO_4$ does not react with the ketones Ph_2CO, $MeC(O)CH_2C(O)Me$, $PhC(O)CH_2C(O)Me$ or the aldehydes $MeCH_2CHO$, PhCHO and $3,4,5\text{-}(OMe)_3C_6H_2CHO$, and 3) $[Au(NH_3)(PAr_3)]ClO_4$ does not react with $MeC(O)CH_2C(O)Me$. In all these reactions, no evidence of the formation of imino species could be obtained. Therefore, substituents attached to the carbonyl groups with inductive effect lower than that of Me (H, aryl, MeC(O)) prevent the condensation.

When complexes **1a** or **1b** were treated with an equimolar amount of the corresponding [Au(acac)L] in an attempt to synthesize complexes $[(AuL)_2(\mu\text{-}N{=}CMe_2)]ClO_4$, mixtures were obtained that we could not separate. According to ^{31}P NMR spectral data, the dinuclear complexes seem to form ($\delta = 30.28$ (s, L = PPh_3) or 26.26 (s, L = PAr_3)) but they

partially hydrolyze to produce $[(AuL)_2(\mu\text{-}NH_2)]ClO_4$ ($\delta =$ 30.75 (L = PPh_3), 26.66 (s, L = PAr_3)) and $[\{Au(PAr_3)\}_4(\mu_4\text{-}N)]ClO_4$ ($\delta = 19.89$).[39]

Complexes $[Au(NH{=}CMe_2)_2]X$ (X = ClO_4 (**6**), OTf (**6′**)) were obtained in good yields by stirring $[Au(NH_3)_2]X$ (X = ClO_4 or OTf)[39] in acetone for five days (Scheme 3). The

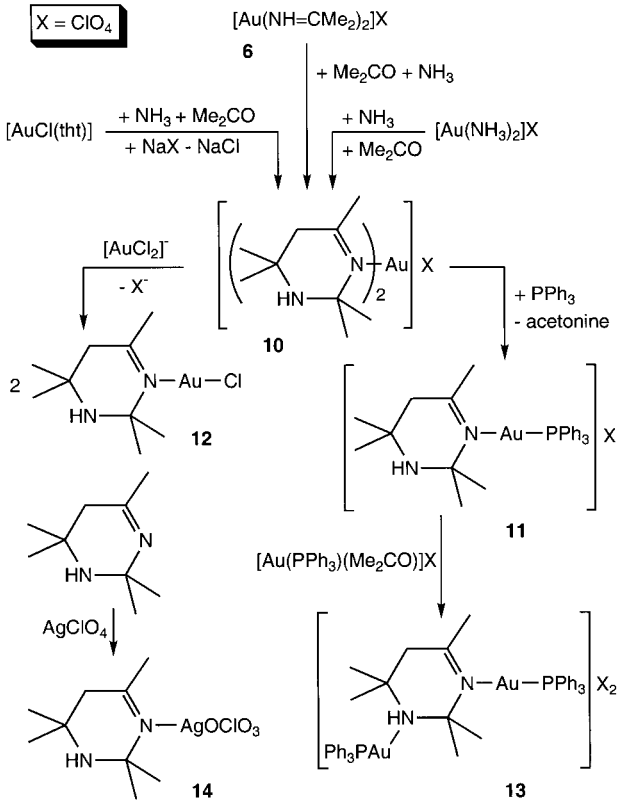


Scheme 3. Synthesis of ketimino gold(I) complexes $[Au(NH{=}CMe_2)_2]X$ (X = ClO_4 (**6**), OTf (**6′**)) from $[Au(NH_3)_2]X$ in acetone.

^{1}H NMR spectrum of the reaction mixture after three days of stirring showed the resonances corresponding to complex **6** along with three other resonances at $\delta = 2.35$ (d, $^4J(H,H) =$ 1.4 Hz), 2.41 (s) and 4.51 (s, br), which could correspond to the Me group *trans* to hydrogen, the Me group *trans* to gold and the NH_3 ligand, respectively, in the intermediate complex $[Au(NH{=}CMe_2)(NH_3)]ClO_4$, which we could not isolate. We attempted the synthesis of **6** from acetone solutions of $NaClO_4$ and $[Au(NH_3)_2]Cl$[39] but no reaction was observed, probably because of the low solubility of this complex in acetone. The reactions between NH_4ClO_4 and $Q[Au(acac)_2]$ (Q = NMe_4, PPN) (2:1, in acetone) produced **6** or **6′** in a much shorter time (3 h), thus proving that these reactions do not involve $[Au(NH_3)_2]^+$ as an intermediate. Rather, intermediates such as $[Au(acac)(NH_3)]$, $[Au(acac)(NH{=}CMe_2)]$ and $[Au(NH{=}CMe_2)(NH_3)]^+$ could be involved. Unfortunately, this is not a convenient route to **6** since separation of the by-product $QClO_4$ has proved very difficult. Single crystals of **6′** (see Figure 2) grew in an attempt to grow crystals of $[Au(NH_3)_2]OTf$ by the liquid diffusion method using acetone/Et_2O.

The complex $[AuCl(NH{=}CMe_2)]$ (**7**) was obtained by metathesis between equimolar amounts of **6** and $PPN[AuCl_2]$[37] in acetone (Scheme 3). Extracting the crude product with a mixture of acetone and Et_2O, in which only **7** dissolved, led to the separation of the by-product $PPNClO_4$. When complex **6** or **7** was treated with an equimolecular amount of $PhICl_2$, oxidative addition of chlorine took place to give $[AuCl_2(NH{=}CMe_2)_2]ClO_4$ (**8**) or $[AuCl_3(NH{=}CMe_2)]$ (**9**), respectively (Scheme 3). These are the first gold(III) complexes with a noncyclic ketimine.

Synthesis of acetonino complexes of gold(I) and silver(I): We have previously described the synthesis of $[Au(NH_3)_2]Cl$ by bubbling NH_3 through an acetone solution of [AuCl(tht)] (tht = tetrahydrothiophene).[39] This complex does not react with $NaClO_4$ to give $[Au(NH_3)_2]ClO_4$, nor with acetone to give $[Au(NH{=}CMe_2)_2]Cl$ or **7**, probably because of its insolubility in all common solvents. However, it does react with $AgClO_4$ in acetone to produce insoluble AgCl and $[Au(NH_3)_2]ClO_4$. We presumed that this complex could be better obtained in the one pot reaction of NH_3 with [AuCl(tht)] in acetone in the presence of $NaClO_4$. However, when NH_3 was bubbled (15 min) through an acetone solution containing equimolar amounts of [AuCl(tht)] and $NaClO_4$ and the resulting suspension was further stirred for 1 h, the complex $[Au(acetonine)_2]ClO_4$ (**10**) (Scheme 4) was obtained



Scheme 4. Synthesis of acetonino gold(I) and silver(I) complexes from the reaction of various gold(I) complexes with NH_3 and acetone.

as the major product (88%). A small amount of $[Au(NH_3)_2]Cl$ precipitated during the reaction and was removed by filtration. However, neither the desired complex $[Au(NH_3)_2]ClO_4$ nor its reaction product with acetone (**6**) were even detected among the final products. If such two complexes were formed in the reaction, the result would be the same because, as we have independently proved, **10** is also formed when NH_3 is bubbled through their acetone solutions. The same result is

0947-6539/01/0703-0640 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 3

obtained when NH_3 was bubbled through acetone (20 mL) for 15 min and then $[Au(NH_3)_2]ClO_4$ (ca.1 mmol) added and the resulting mixture was stirred for 1 h. According to all these experiments it seems that the acetonine ligand forms on bubbling NH_3 through acetone and replaces not only the labile tht ligand but also the chloro ligand in [AuCl(tht)], NH_3 in $[Au(NH_3)_2]ClO_4$ or acetimine in the possible intermediate species $[Au(NH_3)(NH{=}CMe_2)]ClO_4$ or $[Au(NH{=}CMe_2)_2]$-ClO_4. The rapid formation of **10** compared to that of $[Au(NH{=}CMe_2)L]^+$ or $[Au(NH{=}CMe_2)_2]^+$ (1 h, 2–5 h, 5 days, respectively) means that acetimine rapidly forms and condenses to acetonine in the reaction between ammonia and acetone, whereas formation of acetimine from ammonia coordinated to gold(I) is a slow process, especially in the case of both ammonia molecules in $[Au(NH_3)_2]^+$.

The reaction of **10** with triphenylphosphane in 1:1 or 1:2 molar ratio results in the displacement of one or both acetonine ligands to give $[Au(acetonine)(PPh_3)]ClO_4$ (**11**) or $[Au(PPh_3)_2]ClO_4$, respectively. Complex **11** was also obtained, along with other unidentified species, when NH_3 was bubbled through acetone solutions of **1a** or $[Au(PPh_3)(Me_2CO)]ClO_4$. The metathesis reaction of **10** and $PPN[AuCl_2]$ produces [AuCl(acetonine)] (**12**) and $PPNClO_4$, which can be separated easily because of the solubility of **12** in Et_2O. Complex **12** was also obtained in similar yield when [AuCl(tht)] and acetonine (1.2:1) were allowed to react in acetone for 30 min. In contrast, the reaction between equimolecular amounts of **11** and $[Au(PPh_3)(Me_2CO)]ClO_4$ leads to the displacement of the labile acetone ligand by the uncoordinated amine function present in **11** to give the dinuclear complex $[(AuPPh_3)_2(\mu$-acetonine$)](ClO_4)_2$ (**13**) (Scheme 4).

The reaction of acetonine and $AgClO_4$ (1.1:1) in Et_2O caused immediate precipitation of the complex $[Ag(acetonine)(OClO_3)]$ (**14**), which was isolated by filtration in almost quantitative yield. Complexes **10**–**14** are the first coordination complexes containing acetonine.

Crystal structure of 5: This complex was previously described by us[38] and has now been used as the starting material for the synthesis of **4**. In an attempt to grow single crystals of **4** by the liquid diffusion method using dichloromethane and *n*-hexane, crystals of **5** suitable for an X-ray diffraction analysis were obtained as the result of hydrolysis. The crystal structure of **5** (Figure 1) consists of $[Au(NH_2Ar)(PPh_3)]^+$ ions and triflate anions. The cation shows the gold atom in an almost linear environment (P-Au-N 178.10(11)°) with Au–N (2.112(4) Å) and Au–P (2.2376(12) Å) bond lengths similar to those found in the related complexes $[Au(NMe_3)(PPh_3)]ClO_4 \cdot CH_2Cl_2$[38] (2.108(7) and 2.231(2) Å), [Au(quinuclidine)$(PPh_3)]BF_4$[40] (2.11(1) and 2.240(4) Å) and $[Au(NH_2tBu)L]BF_4$ ($L = PMe_3$, $PMePh_2$)[41] (2.105(8)–2.11(1) and 2.235(3)–2.236(3) Å). The last two complexes are the only ones related with **5** that contain a primary amine. In spite of the tendency of gold(I) complexes to aggregate through short Au···Au contacts (aurophilicity),[42–44] such contacts are absent in **5**. The size of the ligands attached to the gold atom is very important for the existence of such a weak interaction. In fact, the smaller PMe_3 ligand in $[Au(NH_2tBu)(PMe_3)]BF_4$, as compared with PPh_3 in **5**, allows a short Au···Au contact (3.047(1) Å).[41]

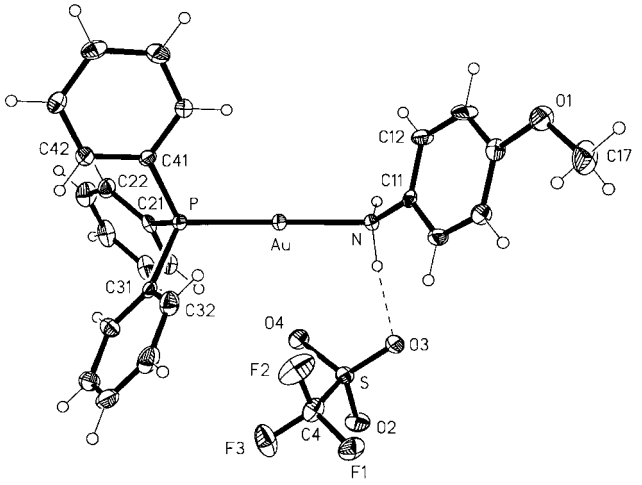


Figure 1. Crystal structure of **5**. Selected bond lengths [Å] and angles [°]: Au–N 2.112(4), Au–P 2.2376(12); N-Au-P 178.10(11), Au-N-C11 116.9(3).

Instead, two hydrogen bonds $NH\cdots OSO_2CF_3$ are formed that link two ion pairs across an inversion centre (N–H01···O3 with H···O 1.89(3) Å, NH···O 174(4)° and N–H02···O4 with H···O 1.92(3) Å, NH···O 155(3)°, operator $-x, 1-y, 1-z$). The dimers are further linked into chains by a nonclassical hydrogen bond C35–H35···O2 with H···O 2.48 Å, C–H···O 137°.

Crystal structure of 6′: The crystal structure of this complex was already preliminarily reported[22] by us (Figure 2) and shows as the main features: 1) two independent formula units

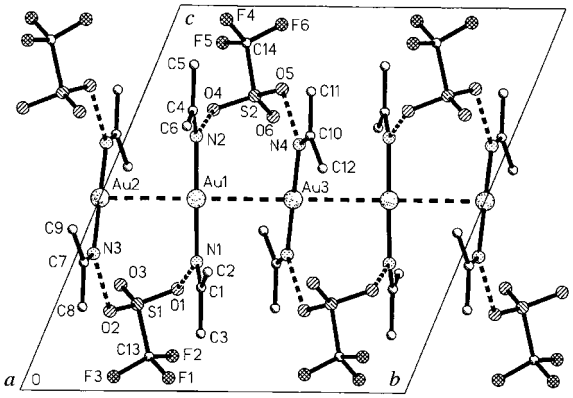


Figure 2. Crystal structure of **6′** projected down the *x* axis. Only the asymmetric unit is numbered. H atoms are omitted for clarity. Secondary interactions (aurophilic and hydrogen bonds) are indicated by broken bonds. Selected bond lengths [Å] and angles [°]: Au1–N1 2.017(5), N1–C1 1.285(8), Au1–N2 2.018(2), N2–C4 1.271(7), Au1–Au2 3.1663(5), Au1–Au3 3.1705(5); N1-Au1-N2 178.7(2), Au2-Au1-Au3 153.346(10), other N-Au-N and Au-Au-Au 180° by symmetry.

but three independent gold atom positions (Au2 and Au3 lie on inversion centers); 2) a polymeric chain of $[Au(NH{=}CMe_2)_2]^+$ ions formed through short Au···Au contacts (3.1663(5), 3.1705(5) Å) with Au2-Au1-Au3 angles of 153.364(10)° and all other Au-Au-Au angles of 180° by symmetry; 3) linear disposition of the AuN_2 moieties (N1-Au1-N2, 178.7(2)° and all other N-Au-N angles 180° by

symmetry) with Au–N bond lengths (2.017(5), 2.018(2) Å) similar to those found in Au^I complexes with the NH=CPh_2 ligand (in the range 1.985–2.07 Å),[10, 13] and 4) four independent hydrogen bonds formed between the triflate anions and the NH groups of the acetimine ligands (N···O 2.89–2.91 Å and N–H···O 158–167°). As far as we know, there are only two other complexes in which Au···Au contacts are established among cationic species, the pentameric [Au(pyridine-2-thione)$_2$]ClO_4[45] and the dimeric [Au(NH_2tBu)(PMe_3)]BF_4.[41] In complex **6′** the additional hydrogen bond interactions could be the factor supporting the polymerization.

Only three crystal structures of acetimine complexes are available for comparison with that of **6′**.[10, 13, 14] The acetimino ligands present in **6′**, in [$AlCl_3$(NH=CMe_2)],[14] and in [W(PhC≡CPh)$_3$(NH=CMe_2)][10] show almost identical C=N bond lengths (**6′**: 1.285(8), 1.271(7) Å; [$AlCl_3$(NH=CMe_2)], 1.282(4) Å; [W(PhC≡CPh)$_3$(NH=CMe_2)], 1.284(7) Å) and angles around the iminic carbon atom [**6′**: Me-C-Me, 116.9(6), 119.3(6)°; Me-C-N, 120.4(7)°, 120.3(7)°, 121.6(6)° 121.5(6)°; [$AlCl_3$(NH=CMe_2)], Me-C-Me 117.7(3)°, Me-C-N, 120.5(3)°, 121.8(3)°; [W(PhC≡CPh)$_3$(NH=CMe_2)]: Me-C-Me, 116.6(5)°; Me-C-N, 120.6(5)°, 122.6(5)°]. However, the imino ligands present in [Ru(NH=CMe_2)$_2$(bipy)$_2$](PF_6)$_2$[13] display shorter C=N bond lengths (1.159 Å), a narrower Me-C-Me bond angle (99°), and Me-C-N angles of 148° and 113°.

Crystal structure of [Au(acetonine)$_2$]ClO_4 (10): The crystal structure of this complex was already preliminarily reported by us (Figure 3).[1] Neither acetonine complexes nor X-ray crystal studies on acetonine or any other 2,2,4,4,6-substituted tetrahydropyrimidine have been previously reported. The structure of **10** consists of [Au(acetonine)$_2$]$^+$ ions and perchlorate anions (see Figure 3a). In the cation, the gold atom lies on an inversion center. The acetonine ring is on a half-chair conformation with the atom C(3) 0.62 Å out of the main plane (mean deviation 0.005 Å). The Au–N bond length found in **10** (2.040(5) Å) is similar to those found in **6′** (2.017(5), 2.018(2) Å) or other complexes containing Au–N(sp^2) bonds (range 1.985–2.07 Å).[10, 13] The bond lengths in the acetonine ring are normal when compared with those found in compounds with similar hybridization and bond order.[46] Thus, 1) N1=C1 1.297(8) Å is similar to C(sp^2)=N(sp^2) in furoxan (1.316 Å), 2) C1–C2, 1.502(8) Å and C2–C3 1.528(7) Å are similar to C(sp^2)–C(sp^3) (1.506 Å) and C(sp^3)–C(sp^3) (1.535 Å), respectively, found in cyclohexene, 3) C3–N2 1.469(7) Å and C4–N2 are similar to the mean distance found for C(sp^3)–N(sp^3) (1.469 Å), and 4) C4–N1 1.510(7) is in the range found for various C(sp^3)–N(sp^2) (1.454–1.479 Å). A zigzag chain perpendicular to the *bc* plane is formed through a N(2)–H(2)···O(2) hydrogen bond (N(2)···O(2) 3.225(9), H(2)···O(2) 2.42(3) Å, and N(2)–H(2)···O(2) 154(5)° for the main component of the disordered perchlorate anion (72% refined occupancy)). A linear arrangement of the gold atoms along the *c* axis has been found (see Figure 3b).

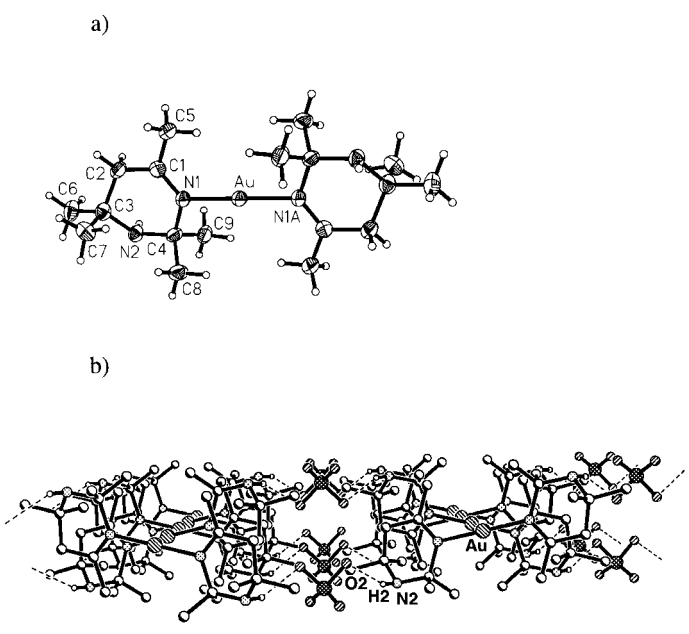


Figure 3. a) Crystal structure of the cation **10** showing the atom numbering scheme. Selected bond lengths [Å] and angles [°]: Au–N1 2.040(5), N1–C1 1.297(8), C1–C2 1.502(8), C2–C3 1.528(7), C3–N2 1.469(7), N2–C4 1.474(7), C4–N1 1.510(7); N1-C1-C2 122.1(5), C1-C2-C3 112.6(5), C2-C3-N2 108.0(4), C3-N2-C4 118.3(4), N2-C4-N1 113.6(4), C4-N1-C1 122.6(5). b) Packing diagram along the *c* axis of compound **10**·ClO_4 showing the hydrogen bond N2CH2···O2 [N2···O2 3.26(1), H2···O2 2.46(4), N2–H2···O2 157(5)°]

NMR, IR and FAB spectra: The ^{1}H NMR spectrum of NH=CMe_2 (in $CDCl_3$) has been reported[6] to show one singlet at $\delta = 1.93$ for both Me groups while the resonance for the NH proton was not observed. The ^{1}H NMR spectra (see Experimental Section) of those complexes containing this ligand show the NH resonance as a broad singlet ($\delta = 10.15$ (**1a**), 10.36 (**1b**), 10.17 (**6**), 10.28 (**6′**), 9.42 (**7**)) or as a 1:1:1 triplet ($\delta =$ 8.55 (**9**), ^1J(H,N) = 62 Hz). We have previously observed ^{1}H coupling to ^{14}N in [Au(NH_3)$_2$]$^+$ although with a lower ^1J(H,N) value (37–39 Hz) as expected for the lower s character of the hybrids at N.[39]. The NH resonance is absent in the CD_3OD-^{1}H NMR spectrum of **8** probably because of H/D interchange. In complexes **2a** and **2b**, two NH resonances ($\delta = 9.93$, 10.10 (**2a**); 10.12, 10.31 (**2b**)) are observed because of the presence of two isomers (see below).

The spectra of the acetimino gold complexes show also two additional resonances indicating inequivalent Me groups, arising from restricted rotation around the N=C bond at room temperature. The resonance at lower field ($\delta = 2.43$ (**1a**), 2.38 (**1b**), 2.44 (**6**), 2.46 (**6′**), 2.32 (**7**), 2.80 (**8**), 2.64 (**9**)) is a singlet that we assign to the Me group *trans* to the $AuPR_3$ moiety, while that at higher field is a somewhat broadened singlet ($\delta = 2.37$ (**1a**), 2.71 (**8**), 2.56 (**9**)) or a doublet ($\delta = 2.37$ (**1b**), ^4J(H,H) = 1.2 Hz; 2.38 (**6**), ^4J(H,H) = 1.2 Hz; 2.39 (**6′**), ^4J(H,H) = 1.2 Hz; 2.24 (**7**), ^4J(H,H) = 1.8 Hz) that we assign to the Me group *trans* to the hydrogen atom of the NH group, based on irradiation at the NH proton frequency. We have carried out a variable-temperature ^{1}H NMR spectroscopy study for complex **1a** and found the coalescence temperature and the free energy of activation for the rotation around the C=N bond to be 52.5 (±0.15) °C and 13.22 (±0.1) Kcal mol^{-1}, respectively. At 60 °C the spectrum shows a singlet at $\delta = 2.38$

0947-6539/01/0703-0642 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 3

for both equivalent Me groups. In the case of **1b** free rotation is observed above 55 °C.

The ^{1}H NMR spectra of complexes **2** containing the NH=C(Me)Et ligand reveal the presence in solution of a mixture (**2a** 1.7:1, **2b** 1.3:1) of the two possible isomers. According to the assignment made for complexes **1**, the most abundant isomer for complexes **2a** and **2b** is that with the Me group *trans* to the $AuPR_3$ moiety. The spectrum of **2a** is contaminated with trace amounts of the hydrolysis product $[Au(PPh_3)(NH_3)]ClO_4$,[39] presumably formed from traces of water in the deuterated solvent.

Complexes **3** and **4** contain the ligands N(R)=CMe_2 (R = Me, Ar), respectively, and show resonances expected for the R group attached to nitrogen and also two separate resonances for both methyl groups of the CMe_2 moiety; one of them is a singlet ($\delta = 2.26$ (**3**), 2.27 (**3′**), 2.16 (**4**)) while the other is a doublet ($\delta = 2.62$ (**3**, **3′**), $^5J(P,H) = 1.2$ Hz) or a singlet ($\delta = 2.82$ (**4**)). The $^5J(P,H)$ coupling constant in these complexes is equal or very close to the $^4J(H,H)$ value found in **1b**, **6**, **6′**, and **7** (1.8 Hz). When the spectrum of **4** was measured several hours after dissolving the sample, it showed the presence of a small amount of **5**[38] which must form by hydrolysis, as was observed when single crystals of **5** were obtained from solutions of **4**. The $^{31}P\{^1H\}$ NMR spectra of complexes **1–4** show a singlet resonance for the PR_3 ligand at around $\delta = 26$ (R = Ar) or in the range $\delta = 28.7-30$ (R = Ph) (see Experimental Section).

The ^{1}H NMR spectra of the acetonino complexes **10–14** (see Experimental Section) show the expected resonances that we have assigned by comparison with those of the free ligand, assuming that in all these complexes the metal center is coordinated to N1 (see Scheme 1) as shown in the crystal structure of **10**. In fact the maximum and minimum differences with respect to the corresponding resonances in the free ligand correspond to the Me group on C6 ($\delta = 1.96$ (acetonine), 2.53 (**10**), 2.57 (**11**), 2.48 (**12**), 2.70 (**13**), 2.37 (**14**)) and the Me groups on C4, ($\delta = 1.12$ (acetonine), 1.21 (**10**), 1.21 (**11**), 1.19 (**12**), 1.74, 1.78 (**13**), 1.21 (**14**)), while the opposite should be observed if coordination took place through N3. All resonances in the spectra of complexes **10–12** and **14** are singlets in spite of the chiral nature of N3, indicating a fast inversion process. The ^{1}H NMR spectrum of **13** shows an AB system for the CH_2 protons and one singlet for each of the four different Me groups. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet for each of the $AuPPh_3$ groups. Both spectra prove that coordination of the $AuPPh_3$ groups occurs at different nitrogen atoms. The $^{31}P\{^1H\}$ NMR spectrum of **11** shows a singlet at $\delta = 29.29$. The $^{13}C\{^1H\}$ NMR spectra of complexes **1a**, **1b**, **2a**, **2b**, and **10** were measured (see Experimental Section) and support the proposed structures.

The vibrational spectra of NH=CMe_2 show two weak NH bands (Raman, 3326 and 3260 cm^{-1}) and also two C=N bands (IR, 1658, 1670 sh cm^{-1}).[6] With the exception of **3**, **4**, and **13**, which do not have NH groups, all the complexes described here show one medium to strong broad ν(NH) band in the 3195–3312 cm^{-1} region (3213 (**1a**), 3230 (**1b**), 3230 (**2a**), 3249 (**2b**), 3248 (**6**), 3215 (**6′**), 3219 (**7**), 3195 (**8**), 3312 (**9**; in CH_2Cl_2 solution), 3305 (**10**), 3297 (**11**), 3291 (**12**), 3215 (**14**) cm^{-1}). The monoimino complexes **1–4** show one medium to strong ν(C=N) band in the 1620–1670 cm^{-1} region (1638 (**1a**), 1646 (**1b**), 1640 (**2a**), 1641 (**2b**), 1651 (**3**), 1644 (**3′**), 1627 (**4**) cm^{-1}) while the bis-imino complexes **6** and **6′** show two ν(C=N) bands in the same region (**6**: 1660, 1643; **6′**: 1663, 1647 cm^{-1}). However, complexes **7** and **9** show two ν(C=N) bands (**7**: 1659, 1643, **9**: 1670, 1650 cm^{-1} (in dichloromethane solution)) in spite of having only one imino function. Schmidbaur et al. have reported[19, 47] that complexes related to **6** and **7**, the isomers $[Au(imine)_2][AuCl_2]$ and [AuCl(imine)] (imine = R_2C=NH, R = Ph, NMe_2), are in equilibrium in solution. In our case, an equilibrium between **7** and $[Au(NH=CMe_2)_2][AuCl_2]$ can be ruled out because of the solubility of **7** in Et_2O and its low molar conductivity in acetone (7 $\Omega^{-1}cm^2mol^{-1}$). The acetonino complexes **10–14** show one ν(C=N) band (**10**: 1629, **11**: 1638, **12**: 1639, **13**: 1642, **14**: 1651 cm^{-1}).

The chloro complexes **7** and **8** show one ν(AuCl) band at 342 and 344 cm^{-1}, respectively. Complex **9** could not be suspended in Nujol, so its IR spectrum was measured in a CH_2Cl_2 solution. The low energy region of the spectrum is very noisy, preventing any assignment. The *trans* geometry of complex **12** is supported by the single ν(AuCl) band at 374 cm^{-1}. The cationic derivatives **1–6**, **8**, **9**, **11**, and **13** show bands of the corresponding counterions (ClO_4 at around 1100 and 620 cm^{-1} and OTf at around 1275 cm^{-1}).

The mass spectra (FAB^+) of complexes **1b**, **2a**, **2b**, **8**, and **11**, have been measured (see Experimental Section) and all show the [M^+] peak and other fragments consistent with the proposed stoichiomeries.

Conclusion

The unstable acetimine can be stabilized as a ligand coordinated to gold(I) or gold(III). Gold(I) complexes, $[Au(NH=CMe_2)L]^+$, $[Au(NH=CMe_2)_2]^+$, or $[AuCl(NH=CMe_2)]$ are prepared by reacting acetone with aminegold(I) complexes ($[Au(NH_3)L]^+$ or $[Au(NH_3)_2]^+$) or by reacting $[Au(NH=CMe_2)_2]^+$ with $[AuCl_2]^-$, respectively. Acetimino gold(III) complexes, $[AuCl_2(NH=CMe_2)_2]^+$ or $[AuCl_3(NH=CMe_2)]$, have been obtained by reacting $PhICl_2$ with $[Au(NH=CMe_2)_2]^+$ or $[AuCl(NH=CMe_2)]$, respectively. Bubbling ammonia through acetone leads rapidly to acetonine. If a gold(I) or silver(I) species is present in solution or added after bubbling, complexes with this important compound can be isolated. The X-ray diffraction studies of some of these complexes show interesting hydrogen bonds and aurophilic interactions.

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 16FPCFT-IR spectrophotometer using Nujol mulls between polyethylene sheets except in the case of complex **9**, where the IR spectrum was measured in a dichloromethane solution to avoid massive decomposition. Conductivities were measured with a Philips PW9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, N, and S analyses were carried out with a Carlo Erba 1106 microanalyzer. The NMR spectra were recorded on a Varian Unity

300 MHz spectrometer at room temperature in $CDCl_3$ unless otherwise stated. TMS was used as a reference for the ^1H and $^{13}C\{^1H\}$ NMR spectra and H_3PO_4 was used for $^{31}P\{^1H\}$ NMR spectra. Mass spectra (FAB^+) were measured with a Fisons VG-Autospec spectrometer using 3-nitrobenzyl alcohol (NBA) as the matrix. Unless otherwise stated, the reactions were carried out at room temperature, without any special precautions against daylight or moisture. The solvents were dried using standard methods and freshly distilled, except in the case of *n*-pentane that was used as received. Complexes **6′** and **10** were preliminarily reported by us including a crystal structure.[22]

Warning! Mixtures of perchlorate salts with organic cations may be explosive. Preparations on a larger scale than that reported herein should be avoided.

$[AuCl(tht)]$,[48] $PPN[AuCl_2]$,[37] $[Au(acac)PR_3]$ (R = Ph, Ar),[37, 39] $[Au(NH_2Me)(PPh_3)]Otf$,[39] **5**,[38] $[Au(NH_3)_2]X$ (X = Cl, ClO_4, Otf),[39] and $PhICl_2$,[49] were prepared as previously described.

$[MeNH_3]OTf$ was prepared in 76% yield by bubbling a stream of $MeNH_2$ (obtained by dropwise addition of a concentrated aqueous solution of NaOH to solid $MeNH_2 \cdot HCl$ (from Fluka)) through a solution of HOTf in Et_2O. The white precipitate was filtered and washed with Et_2O. It was dried and stored under nitrogen. The homologous perchlorate salt $[NH_3Me]ClO_4$ was obtained in 61% yield by reacting equimolar amounts of $MeNH_2 \cdot HCl$ and $NaClO_4 \cdot H_2O$ in acetone. Both gave correct elemental analyses.

We have prepared acetonine by bubbling NH_3 through acetone for 15 min, stirring the resulting mixture for three days, and removing the solvent under vacuum below 35 °C. The same semisolid behavior previously described by Bobbit[50] was observed. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS (see Scheme 1 for numbering scheme): $\delta = 1.12$ (s, 6H; Me4), 1.38 (s, 6H; Me2), 1.87 (s, CH_2; 2H), 1.96 (s, 3H; Me6).

$(NH_4)ClO_4$ was purchased from Probus and recrystallized from acetone and Et_2O while MeC(O)Et was purchased from Merck and used as received.

$[Au\{NH{=}CMe_2\}(PR_3)]ClO_4$ (R = Ph (1a), Ar (1b)): An equimolar amount of the corresponding $[Au(acac)PR_3]$ was slowly added to a solution of $(NH_4)ClO_4$ (**1a:** 60 mg, 0.51 mmol; **1b:** 45 mg, 0.38 mmol) in acetone (15 mL). The reaction mixture was stirred at room temperature for 2 (**1a**) or 2.5 (**1b**) h and filtered through celite. The solution was concentrated (1 mL) under vacuum and Et_2O (15 mL) added. An oily material formed, which was washed with Et_2O (3×10 mL). Recrystallization from acetone (1 mL)/Et_2O (15 mL) gave **1a** or vacuum drying for 4 h gave **1b**. Both complexes are white solids.

1a: Yield: 270 mg, 86%; decomposition point 172 °C; ^1H NMR (200 MHz): $\delta = 2.37$ (s, br 3H; Me), 2.43 (s, 3H; Me), 7.42–7.65 (m, 15H; Ph), 10.15 (s, br, 1H; NH); $^{13}C\{^1H\}$ NMR (50 MHz): $\delta = 28.41$ (s; Me), 29.36 (s; Me), 127.28 (d, $^1J(C,P) = 64$ Hz; *ipso*-Ph), 129.32 (d, $^3J(C,P) = 9.9$ Hz; *m*-Ph), 132.37 (d, $^4J(C,P) = 2.6$ Hz; *p*-Ph), 133.80 (d, $^2J(C,P) = 13.5$ Hz; *o*-Ph,), 191.25 (s; C=N); $^{31}P\{^1H\}$: $\delta = 29.7$ (s); IR (Nujol): $\tilde{\nu} = 3213$ (NH), 1638 (C=N) cm^{-1}; Λ_M (acetone, 6.43×10^{-4} M): 126 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_{21}H_{22}AuClNO_4P$: C 40.96, H 3.60, N 2.27; found: C 40.91, H 3.47, N 2.24.

1b: Yield: 174 mg, 65%; m.p. 74 °C; ^1H NMR: $\delta = 2.37$ (d, $^4J(H,H) = 1.2$ Hz, 3H; Me), 2.38 (s, 3H; Me), 3.86 (s, 9H; OMe), 6.97–7.47 (m, 12H, AA′BB′X system; Ar), 10.36 (s, br, 1H; NH); $^{13}C\{^1H\}$ NMR (50 MHz): $\delta = 28.31$ (d, $^4J(C,P) = 4$ Hz; Me), 29.26 (s; Me), 55.49 (s; MeO), 115.37 (d, $^3J(C,P) = 32$ Hz; *o*-C_6H_4), 118.94 (d, $^1J(C,P) = 75$ Hz; *ipso*-C_6H_4), 135.50 (d, $^3J(C,P) = 15$ Hz; *m*-C_6H_4), 162.61 (d, $^4J(C,P) = 2$ Hz; *p*-C_6H_4), 190.67 (s; C=N); $^{31}P\{^1H\}$: $\delta = 25.99$ (s); IR (Nujol): $\tilde{\nu} = 3230$ (NH), 1646 (C=N) cm^{-1}; Λ_M (acetone, 2.15×10^{-4} M): 110 $\Omega^{-1} cm^2 mol^{-1}$; MS ($FAB^+$): *m/z* (%): 606.38 (100) [M^+], 549.34 (56) [$AuPAr_3$], 58.10 (58) [NH_2CMe_2]; elemental analysis calcd (%) for $C_{24}H_{28}AuClNO_7P$: C 40.84, H 3.99, N 1.98; found: C 40.75, H 3.87, N 1.95.

$[Au\{NH{=}C(Me)(Et)\}(PR_3)]ClO_4$ (R = Ph (2a), Ar (2b)): An equimolar amount of the corresponding $[Au(acac)PR_3]$ was slowly added to a suspension of $(NH_4)ClO_4$ (**2a:** 60 mg, 0.51 mmol; **2b:** 52 mg, 0.44 mmol) in MeC(O)Et (15 mL). The reaction mixture was stirred at room temperature for 1 h (**2a**) or 5 h (**2b**) and filtered through celite. The solution was concentrated (1 mL) and Et_2O (15 mL) added to give a white oil which was washed with Et_2O (3×15 mL). In the case of **2a** it was recrystallized from dichloromethane (2 mL) and Et_2O (20 mL) and dried under vacuum for 3 h, while **2b** was obtained upon drying the oily material under vacuum for 4 h.

2a: Yield: 185 mg, 58%; m.p. 77 °C; ^1H NMR (mixture of two isomers in 1.7:1 molar ratio), the more abundant isomer: $\delta = 1.22$ (t, $^3J(H,H) = 7.5$ Hz, 3H; CH_2Me), 2.41 (s, 3H; CMe), 2.59 (q, 2H; CH_2Me), 9.93 (s, br, 1H; NH); the less abundant isomer: $\delta = 1.31$ (t, $^3J(H,H) = 7.5$ Hz, 3H; CH_2Me), 2.32 (s, 3H; C*Me*), 2.65 (q, 2H; CH_2Me), 7.50 (m, 30H; Ph), 10.10 (s, 1H, br; NH); $^{13}C\{^1H\}$ NMR (50 MHz): $\delta = 9.59$ (s; CH_2Me), 11.29 (s; CH_2Me), 20.0 (s; Me), 27.67 (s; Me), 34.64 (s; CH_2Me), 35.99 (s; CH_2Me), 127.36 ($^1J(C,P) = 64$ Hz; *ipso*-Ph), 129.45 (d, $^3J(C,P) = 12$ Hz; *m*-Ph), 132.08 (s; *p*-Ph), 134.07 (d, $^2J(C,P) = 13$ Hz; *o*-Ph), 194.73 (s; *C*=N), 195.35 (s, *C*=N); $^{31}P\{^1H\}$: $\delta = 29.98$ (s); IR (Nujol): $\tilde{\nu} = 3230$ (NH), 1640 (C=N) cm^{-1}; Λ_M (acetone, 4.19×10^{-4} M): 124 $\Omega^{-1} cm^2 mol^{-1}$; MS ($FAB^+$): *m/z* (%): 530.48 (100) [M^+], 459.34 (76) [$AuPPh_3$], 721.34, (17) [$Au(PPh_3)_2$]; elemental analysis calcd (%) for $C_{22}H_{24}AuClNO_4P$: C 41.95, H 3.84, N 2.22; found: C 41.51, H 3.58, N 2.16.

2b: Yield: 216 mg, 68%; m.p. 78 °C; ^1H NMR (mixture of two isomers): $\delta = 1.21$ (t, $^3J(H,H) = 7$ Hz, 3H; CH_2Me), 1.25 (t, $^3J(H,H) = 7$ Hz, 3H; CH_2Me), 2.34 (s, br, 3H; Me), 2.40(s, 3H; Me), 2.60 (q, 2H; CH_2Me), 2.65 (q, 2H; CH_2Me), 3.85 (s, 18H; OMe), 6.98–7.54 (m, 24H, AA′BB′X system; Ar), 10.12 (s, br, 1H; NH), 10.31 (s, br, 1H; NH); $^{13}C\{^1H\}$ NMR (50 MHz): $\delta = 9.75$ (s; CH_2Me), 11.32 (s; CH_2Me), 26.03 (s; Me), 27.53 (s; Me), 34.78 (s; CH_2Me), 35.97 (s; CH_2Me), 55.73 (s; OMe), 115.17 (m; *o*-C_6H_4), 119.07 (d, $^1J(C,P) = 70$ Hz; *ipso*-C_6H_4), 119.73 (d, $^1J(C,P) = 67$ Hz; *ipso*-C_6H_4) 135.27 (m; *m*-C_6H_4), 162.60 (m; *p*-C_6H_4), 193.96 (s, C=N), 194.55 (s, C=N); $^{31}P\{^1H\}$, 25.97 (s); IR (Nujol): $\tilde{\nu} = 3249$ (NH), 1641 (C=N) cm^{-1}; Λ_M (acetone, 3.83×10^{-4} M): 128 $\Omega^{-1} cm^2 mol^{-1}$; MS ($FAB^+$): *m/z* (%): 901.40 (22) [$Au(PAr_3)_2$], 620.46 (56) [M^+], 549.4 (100) [$AuPAr_3$], 245.15 (54) [PAr_2]; elemental analysis calcd (%) for $C_{25}H_{30}AuClNO_7P$: C 41.71, H 4.20, N 1.94; found: C 41.32, H 4.08, N 1.58.

$[Au\{N(Me){=}CMe_2\}(PPh_3)]ClO_4$ (3): Method A: $[Au(acac)(PPh_3)]$ (275 mg, 0.49 mmol) was added to a solution containing $(MeNH_3)ClO_4$ (59 mg, 0.49 mmol) in acetone (15 mL), and the resulting mixture was stirred for 2.5 h. After filtering, the solution was concentrated (2 mL), and Et_2O (20 mL) added to give a white solid that was recrystallized from acetone and Et_2O and then from dichloromethane and Et_2O, washed with Et_2O (2×15 mL), and air dried.

$[Au\{N(R){=}CMe_2\}(PPh_3)]OTf$ [R = Me (3′) Ar (4)]: Method B: Solutions of complexes $[Au(NH_2R)(PPh_3)]OTf$[38, 39] (R = Me (123 mg, 0.25 mmol), Ar (150 mg, 0.21 mmol)) in acetone (15 mL) were stirred for 2 h and then filtered through celite. The filtrates were concentrated (1 mL), Et_2O added (20 mL), and the resulting solids recrystallized twice from acetone and Et_2O to give **3′**, or from acetone and *n*-hexane and then from CH_2Cl_2 and *n*-hexane to give **4**, both as colorless solids. Complex **3′** was also obtained, although in low yield, when method A was followed using $[Au(acac)(PPh_3)]$ and $(NH_3Me)OTf$.

3: Yield: 200 mg, 87%; m.p. 137 °C; ^1H NMR: $\delta = 2.26$ (s, 3H; Me), 2.62 (d, $^5J(P,H) = 1.2$ Hz, 3H; Me), 3.56 (s, 3H; NMe), 7.47–7.61 (m, 15H; Ph); $^{31}P\{^1H\}$, 28.73 (s); IR (Nujol): $\tilde{\nu} = 1651$ (C=N) cm^{-1}; Λ_M (acetone, 5.54×10^{-4} M): 123 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_{22}H_{24}AuClNO_4P$: C 41.95, H, 3.84, N 2.22; found: C 42.06, H 3.72, N 2.11.

3′: Yield: 115 mg, 72%; m.p. 103 °C; ^1H NMR: $\delta = 2.27$ (s, 3H; Me), 2.62 (d, $^5J(P,H) = 1.2$ Hz, 3H; Me), 3.56 (s, 3H; NMe), 7.41–7.61 (m, 15H; Ph); $^{31}P\{^1H\}$, 28.71 (s); IR (Nujol): $\tilde{\nu} = 1644$ cm^{-1} (C=N); Λ_M (acetone, 5.36×10^{-4} M): 127 $\Omega^{-} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_{23}H_{24}AuF_3NO_3PS$: C 40.66, H 3.56, N 2.06, S 4.72; found: C 40.24, H 3.45, N 2.06, S 4.62.

4: Yield: 25 mg, 16%, m.p. 63 °C; ^1H NMR: $\delta = 2.16$ (s, 3H; Me), 2.82 (s, 3H; Me), 3,83 (s, 3H; OCH_3), 6.93–7.21 (m, 4H, AA′BB′ system; Ar), 7.42–7.59 (m, 15H; Ph); $^{31}P\{^1H\}$, 28.89 (s); IR (Nujol): $\tilde{\nu} = 1627$ (C=N) cm^{-1}; Λ_M (acetone, 6×10^{-4} M)): 116 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_{29}H_{28}AuF_3NO_4PS$: C 45.15, H 3.66, N 1.82, S 4.16; found: C 44.84, H 3.50, N 1.90, S 3.71.

$[Au(NH{=}CMe_2)_2]X$ (X = ClO_4 (6), OTf (6′)): A solution of $[Au(NH_3)_2]X$ (X = ClO_4, 323 mg, 1.21 mmol; OTf, 100 mg, 0.26 mmol) in acetone (30 mL) was protected from light and stirred for 5 days. The solution was filtered through $MgSO_4$, concentrated under vacuum (2 mL), and Et_2O (20 mL) added to precipitate a white solid, which was filtered and air-dried.

6: Yield: 389 mg, 78%. Decomposition point 105 °C; ^1H NMR: $\delta = 2.34$ (d, $^4J(H,H) = 1.2$ Hz, 3H; Me), 2.37 (s, 3H; Me); ^1H NMR (200 MHz,

0947-6539/01/0703-0644 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 3

[D_6]acetone): $\delta = 2.38$ (d, 3H; Me), 2.44 (s, 3H; Me), 10.17 (s, br, 1H; NH); IR (Nujol): $\tilde{\nu} = 3248$ (NH), 1660, 1643 (C=N) cm^{-1}; Λ_M (acetone, 5.5×10^{-4} M): 147 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_6H_{14}AuClN_2O_4$: C 17.55, H 3.44, N, 6.82; found: C 17.42, H 3.33, N 6.80.

6′: Yield: 85 mg, 70%. Decomposition point 134 °C; ^{1}H NMR (200 MHz, [D_6]acetone): $\delta = 2.39$ (d, ^4J(H,H) = 1.2 Hz, 3H; Me), 2.46 (s, 3H; Me), 10.28 (s, br, 1H; NH); IR (Nujol): $\tilde{\nu} = 3215$ (NH), 1663, 1647 (C=N) cm^{-1}; Λ_M (acetone, 3.9×10^{-4} M)): 126 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_7H_{14}AuF_3N_2O_3S$: C 18.27, H 3.07, N 6.09, S 6.97; found: C 18.10, H 2.99, N 6.11.

[AuCl(NH=CMe$_2$)] (7): Solid **6** (80 mg, 0.19 mmol) was added to a solution of PPN[$AuCl_2$] (157 mg, 0.19 mmol) in acetone (20 mL). The resulting solution was stirred for 1.5 h, filtered through celite, and the solvent removed under vacuum. The residue was extracted with two portions (26 mL) of a mixture of acetone and Et_2O (1:25), and the extracts filtered through celite to remove insoluble $PPNClO_4$. The solution was concentrated (2 mL) and *n*-hexane added to precipitate **7** as an off-white solid, which was filtered and air-dried. Yield: 68 mg, 60%; m.p. 85 °C; ^{1}H NMR: $\delta = 2.24$ (d, ^4J(H,H) = 1.8 Hz, 3H; Me), 2.32 (s, 3H; Me), 9.42 (s, 1H; NH); IR (Nujol): $\tilde{\nu} = 3219$ (NH), 1659, 1643 (C=N) cm^{-1}; Λ_M (acetone, 7.38×10^{-4} M)): 7 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for C_3H_7AuClN: C 12.45, H 2.44, N 4.84; found: C 12.52; H 2.11; N 4.73.

[AuCl$_2$(NH=CMe$_2$)$_2$]ClO$_4$ (8): To a white suspension of **6** (100 mg, 0.24 mmol) in $CHCl_3$ (10 mL) was added $PhICl_2$ (67 mg, 0.24 mmol). After the mixture had been stirred for 10 min, the resulting yellow suspension was filtered, and the solid washed with a mixture of acetone and Et_2O to give **8** as a yellow solid that was filtered, washed with Et_2O (5 mL) and air dried. Yield: 105 mg, 90%; m.p. 126 °C; ^{1}H NMR (200 MHz, CD_3OD): $\delta =$ 2.709 (s, 3H; Me), 2.799 (s, 3H; Me); IR (Nujol): $\tilde{\nu} = 3195$ (NH), 1667, 1648 (C=N), 374 (AuCl) cm^{-1}; Λ_M (acetone 5.0×10^{-4} M): 180 $\Omega^{-1} cm^2 mol^{-1}$; FAB$^+$ mass spectrum: *m/z* (%) 382 (33) [M^+], 311 (62) [Au(NH=CMe_2)$_2$]; elemental analysis (%) calcd for $C_6H_{14}AuCl_3N_2O_4$: C 14.97, H 2.93, N 5.82; found: C 14.73, H 2.81, N 5.85.

[AuCl$_3$(NH=CMe$_2$)] (9): Solid $PhICl_2$ (104 mg, 0.38 mmol) was added to a solution of **6** (100 mg, 0.35 mmol) in CH_2Cl_2 (5 mL). A yellow solid formed within a few seconds. After the mixture had been stirred for 15 min, the solvent was removed under vacuum, and the residue recrystallized from dichloromethane and *n*-pentane and dried under vacuum for 1 h to give **9** as a yellow solid. Yield: 93 mg, 75%; m.p. 81 °C; ^{1}H NMR: $\delta = 2.56$ (s, 3H; Me), 2.64 (s, 3H; Me), 8.58 [t, ^1J(H, N) = 62 Hz, 1H; NH]; IR (Nujol): $\tilde{\nu} =$ 3312 (NH), 1670, 1650 (C=N) cm^{-1}; Λ_M (acetone, 5×10^{-4} M)): 11 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_3H_7AuCl_3N$: C 10.00, H 1.96, N 3.89; found: C 9.95, H 1.78, N 3.74.

[Au(acetonine)$_2$]ClO$_4$ (10): The precipitation of a white solid was observed when NH_3 was bubbled for 15 min through a solution containing $NaClO_4$ (196 mg, 1.6 mmol) and [AuCl(tht)] (tht = tetrahydrothiophene) (514 mg, 1.6 mmol) in acetone (50 mL). The suspension was stirred for 1 h, the solvent removed under vacuum, and the residue extracted with CH_2Cl_2 (2×50 mL). The combined extracts were filtered through $MgSO_4$, the solution concentrated (1 mL) and Et_2O (25 mL) added. The initial oily product transformed into a solid upon stirring, which was filtered and air-dried to give **10** as a white solid. Yield: 856 mg, 88%; m.p. 112 °C (decomp); ^{1}H NMR: $\delta = 1.21$ (s, 6H; Me4), 1.73 (s, 6H; Me2), 2.46 (s, 2H; CH_2), 2.53 (s, 3H; Me6); ^{13}C{^{1}H} NMR (50 MHz): $\delta = 30.30$ (s; Me4), 31.83 (s; Me6), 32.57 (s; Me2), 43.48 (s; CH_2), 46.84 (s; C4), 76.14 (s; C2), 180.24 (s; C=N); IR (Nujol): $\tilde{\nu} = 3305$ (NH), 1629 (C=N) cm^{-1}; Λ_M (acetone, 5×10^{-4} M): 140 $\Omega^{-1} cm^2 mol^{-1}$; MS (FAB$^+$): *m/z* (%): 506 (100) [M^+], 351 (8) [Au(acetonine)], 98 (31); elemental analysis calcd (%) for $C_{18}H_{36}AuClN_4O_4$: C 35.74, H 6.00, N 9.26; found: C 35.55, H 6.04, N 8.93.

[Au(acetonine)(PPh$_3$)]ClO$_4$ (11): Solid PPh_3 (44 mg, 0.17 mmol) was added to a solution of **10** (100 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 2 h and concentrated under vacuum to 1 mL. Addition of Et_2O (25 mL) produced an oily material that converted into a white solid upon stirring with further additions of Et_2O (2×15 mL). Yield: 106 mg, 90%; m.p. 85 °C (decomp); ^{1}H NMR: $\delta = 1.21$ (s, 6H; Me4), 1.77 (s, 6H; Me2), 2.52 (s, 2H; CH_2,), 2.57 (s, 3H; Me6), 7.45–7.63 (m, 15H; Ph); ^{31}P{^{1}H}, 29.29 (s); IR (Nujol): $\tilde{\nu} = 3297$ (NH), 1638 (C=N) cm^{-1}; Λ_M (acetone, 5×10^{-4} M): 136 $\Omega^{-1} cm^2 mol^{-1}$; MS (FAB$^+$): *m/z* (%): 614 (100) [M^+], 598 (10), 557 (5), 517 (23), 459 (66) [AuPPh$_3$], 183 (17), 154 (10) [acetonine]; elemental analysis calcd (%) for $C_{27}H_{33}AuClN_2O_4P$: C 45.49, H 4.67, N 3.93; found: C 45.32, H 4.42, N 3.64.

[AuCl(acetonine)] (12): To a solution of **10** (200 mg, 0.34 mmol) in CH_2Cl_2 (10 mL), solid PPN[$AuCl_2$] (266 mg, 0.34 mmol) was added, and the reaction mixture stirred for 3 h. It was filtered through $MgSO_4$ and the solution concentrated to dryness. The residue was extracted with Et_2O ($3 \times$ 20 mL), the combined extracts filtered through celite, the solution concentrated under vacuum (1 mL), and *n*-hexane (25 mL) was added to give **12** (167 mg, 63%) as a white solid. Yield: 81 mg, 66%; m.p. 92 °C (decomp); ^{1}H NMR (200 MHz): $\delta = 1.19$ (s, 6H; Me4), 1.72 (s, 6H; Me2), 2.25 (s, 2H; CH_2), 2.48 (s, 3H; Me6); IR (Nujol): $\tilde{\nu} = 3291$ (NH), 1639 (C=N) 344, (AuCl) cm^{-1}; Λ_M (acetone, 5×10^{-4} M): 15 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_9H_{18}AuClN_2$: C 27.96, H 4.69, N, 7.25; found: C 27.70, H 4.50, N 6.87.

[(AuPPh$_3$)$_2$(μ-acetonine)](ClO$_4$)$_2$ (13): A solution of [Au(PPh_3) (Me_2CO)]ClO_4 (obtained by reacting [AuCl(PPh_3)] (115 mg, 0.23 mmol) and $AgClO_4$ (48 mg, 0.23 mmol) in acetone (10 mL) for 10 min under nitrogen atmosphere and filtered to remove AgCl) was added to solid **11** (151 mg, 0.21 mmol) under a nitrogen atmosphere. After the mixture had been stirred for 30 min, the solvent was removed under vacuum, the residue extracted with CH_2Cl_2 (2 mL), the extract filtered through $MgSO_4$, and the solution added dropwise with stirring to Et_2O (25 mL). An oily material formed, which was recrystallized from CH_2Cl_2 and Et_2O to give **13** as a white solid. Yield: 199 mg, 74%; m.p. 151 °C; ^{1}H NMR: $\delta = 1.74$ (s, 3H; Me4), 1.78 (s, 3H; Me4), 2.27 (s, 3H; Me2), 2.31 (s, 3H; Me2), 2.70 (s, 3H; Me6), 2.94, 2.86 (AB system, ^2J(H,H) = 16.5 Hz, 2H; CH_2), 5.89 (d, br, 1H; NH), 7.43–7.56 (m, 30H, Ph); ^{31}P{1H}, 28.89 (s), 29.64 (s); IR (Nujol): $\tilde{\nu} =$ 1642 (C=N) cm^{-1}; Λ_M (acetone, 4.5×10^{-4} M)): 184 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_{45}H_{48}Au_2Cl_2N_2O_8P_2$: C 42.50, H 3.80, N 2.20; found: C 42.15, H 3.68, N 2.21.

[Ag(acetonine)(OClO$_3$)] (14): A solution of acetonine (80 mg, 0.52 mmol) in Et_2O (5 mL) was added dropwise to a solution of $AgClO_4$ (100 mg, 0.48 mmol) in the same solvent (10 mL). A white precipitate formed immediately. After the mixture had been stirred for 15 min, the resulting suspension was filtered and the solid was washed with Et_2O (3×25 mL) and dried under vacuum. Yield: 167 mg, 96%; m.p. 158 °C (decomp); ^{1}H NMR ([D_6]acetone): $\delta = 1.21$ (s, 6H; Me4), 1.63 (s, 6H; Me2), 2.37 (s, 3H; Me6), 2.40 (s, 2H; CH_2); IR (Nujol): $\tilde{\nu} = 3215$ (NH), 1651 (C=N) cm^{-1}; Λ_M (acetone, 5.5×10^{-4} M): 138 $\Omega^{-1} cm^2 mol^{-1}$; elemental analysis calcd (%) for $C_9H_{18}AgClN_2O_4$: C 29.90, H 5.02, N 7.75; found: C 29.93, H 5.12, N 7.40.

X-ray crystal structure analysis of 5: Crystal data: $C_{26}H_{24}AuF_3NO_4PS$, monoclinic, $P2_1/n$, $a = 10.7396(10)$, $b = 16.748(2)$, $c = 15.316(2)$ Å, $\beta =$ 100.247(8)°, $V = 2711.0$ Å^3, $Z = 4$. Data collection: Siemens P4, $T =$ −100 °C, $Mo_{K\alpha}$ radiation, $2\theta_{max}$ 50°, 6282 reflections, 4767 unique. Absorption correction was performed using ψ-scans. Structure refinement: anisotropic on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany), NH was refined using distance restraints, methyl groups were refined as rigid groups and other protons were allowed to ride freely. Final $wR2 = 0.046$, $R1 = 0.027$, $S = 0.85$, max. residual electron density 0.50 e Å^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre under the number CCDC-145572. Copies may be obtained without charge from: CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: +(44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for complexes **6′**[1] and **10**[22] were previously deposited with the CCDC under Nos. 100059 and 182/1322, respectively.

Acknowledgements

We thank the Direccion General de Investigación Científica y Técnica (Project PB97-1047) and the Fonds der Chemischen Industrie for financial support. R. G. would like to thank Ministerio de Educación y Ciencia (Spain) for a Grant.

[1] J. Vicente, M. T. Chicote, R. Guerrero, M. C. Ramírez de Arellano, *Chem. Commun.* **1999**, 1541.

[2] G. M. Robertson, *Imines and their N-Substituted Derivatives: NH, N-R and N-Haloimines*, *Vol. 3*, Pergamon, Oxford (UK), **1995**.

[3] R. C. Mehrotra, *Comprehensive Coordination Chemistry*, *Vol. 2*, Pergamon, Oxford (UK), **1987**.
[4] G. Verardo, A. G. Giumanini, P. Strazzolini, M. Poiana, *Synth. Commun.* **1988**, *18*, 1501.
[5] T. Xu, J. Zhang, J. F. Haw, *J. Am. Chem. Soc.* **1995**, *117*, 3171.
[6] K. Findeisen, H. Heitzer, K. Deehnicke, *Synthesis* **1981**, 702.
[7] D. Sellmann, E. Thallmair, *J. Organomet. Chem.* **1979**, *164*, 337.
[8] P. A. Adcock, F. R. Keene, R. S. Smythe, M. R. Snow, *Inorg. Chem.* **1984**, *23*, 2336.
[9] W. D. Harman, H. Taube, *Inorg. Chem.* **1988**, *27*, 3261.
[10] W. Y. Yeh, C. S. Ting, S. M. Peng, G. H. Lee, *Organometallics* **1995**, *14*, 1417.
[11] R. B. King, W. M. Douglas, *Inorg. Chem.* **1974**, *13*, 1339.
[12] E. O. Fischer, L. Knauss, *Chem. Ber.* **1970**, *103*, 1262.
[13] K.-Y. Wong, C.-M. Che, C.-K. Li, C.-K. Chiu, Z.-Y. Zhou, T. C. W. Mak, *J. Chem. Soc. Chem. Commun.* **1992**, 754.
[14] W. Klingebiel, M. Noltemeyer, H.-G. Schmidt, D. Schmidt-Bäse, *Chem. Ber./Recueil* **1997**, *130*, 753.
[15] D. Czarkie, Y. Shvo, *J. Organomet. Chem.* **1970**, *280*, 123.
[16] T. Rappert, A. Yamamoto, *Chem. Lett.* **1994**, 2211.
[17] M. Aresta, E. Quaranta, A. Dibenedetto, P. Giannoccaro, I. Tommasi, M. Lanfranchi, A. Tiripicchio, *Organometallics* **1997**, *16*, 834.
[18] H. Schmidbaur, W. Schneider, A. Bauer, *J. Chem. Soc. Dalton Trans.* **1997**, 415.
[19] W. Schneider, A. Bauer, A. Schier, H. Schmidbaur, *Chem. Ber./ Recueil* **1997**, *130*, 1417.
[20] Y. Nagel, W. Beck, *Z. Anorg. Allg. Chem.* **1985**, *529*, 57.
[21] J. Strähle, in *Gold: Progress in Chemistry, Biochemistry and Technology*, (Eds.: H. Schmidbaur), Wiley, Chichester (UK) **1999**, p. 311.
[22] J. Vicente, M.-T. Chicote, M.-D. Abrisqueta, R. Guerrero, P. G. Jones, *Angew. Chem.* **1997**, *109*, 1252; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1203.
[23] R. B. Bradbury, N. C. Hancox, H. H. Hatt, *J. Chem. Soc.* **1947**, 1394.
[24] Städeler, *Annalen* **1859**, *111*, 305.
[25] A. Balogh, J. Durmis, K. M., J. Sabados, M. Collak, M. Magura, M. Holko, Cs 235,379, **1987** [*Chem. Abstr.* **1988**, *108*, 167494z].
[26] R. Ballardini, V. Borzatta, M. T. Gandolfi, R. Scrima, *Res. Discl.* **1993**, *354*, 701.
[27] K. Sasaki, O. M., K. Myake, Sumitomo Chemical Co, JP 07,291,931, **1995** [*Chem. Abstr.* **1996**, *124*, 202290j].
[28] G. Shimada, Daicel Chemical Industries, Ltd., JP 03,188,066, **1989** [*Chem. Abstr.* **1992**, *116*, 41319t].
[29] Y. Fukuda, Kyowa Yuka Kk, JP 05,117,242, **1991** [*Chem. Abstr.* **1993**, *119*, 180817d].
[30] I. Dragutan, S. Serban, P. Obloja, D. Nistor, V. Dragutan, Combinatul Petrochimic, Pitesti, Rom. RO 96,131, **1987** [*Chem. Abstr.* **1990**, *113*, 172048q].
[31] I. Dragutan, S. Servan, P. Obloja, D. Nistor, V. Dragutan, Combinatul Petrochimic, Pitesti, Rom. RO 96,132, **1987** [*Chem. Abstr.* **1990**, *113*, 212011f].
[32] G. Goemar, M. Bernhardt, W. Haubold, Leuna-Werke A.-G., DE 4,216,056, **1993** [*Chem. Abstr.* **1994**, *120*, 245138a].
[33] M. Inaba, Y. Inui, Mitsubishi Petrochemical Co., Ltd., JP 01,233,271, **1989** [*Chem. Abstr.* **1990**, *112*, 55627w].
[34] R. Kinishi, M. Kasagi, Yoshitomi Pharmaceutical Industries, Ltd., JP 62,132,859, **1985** [*Chem. Abstr.* **1987**, *107*, 198104f].
[35] K. Sakanashi, Y. Azaki, Yoshitomi Pharmaceutical Industries, Ltd., JP 62,167,763, **1987** [*Chem. Abstr.* **1988**, *108*, 150314t].
[36] Z. Ma, Q. Huang, J. M. Bobbit, *J. Org. Chem.* **1993**, *58*, 4837.
[37] J. Vicente, M. T. Chicote, *Inorg. Synth.* **1998**, *32*, 172.
[38] J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1995**, 1251.
[39] J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, M. C. Ramírez de Arellano, *Inorg. Chem.* **1997**, *36*, 4438.
[40] A. Grohmann, J. Riede, H. Schmidbaur, *Z. Naturforsch. B* **1992**, *47*, 1255.
[41] K. Angermaier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1995**, 559.
[42] J. Vicente, M. T. Chicote, I. Saura-Llamas, M. C. Lagunas, M. C. Ramírez de Arellano, P. González-Herrero, M. D. Abrisqueta, R. Guerrero, in *Metal Clusters in Chemistry, Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim (Germany), **1999**, p. 493.
[43] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391.
[44] H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3.
[45] R. Usón, A. Laguna, M. Laguna, J. Jimenez, M. P. Gómez, A. Sainz, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1990**, 3457.
[46] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 1* **1987**, S1.
[47] W. Schneider, A. Bauer, H. Schmidbaur, *J. Chem. Soc. Dalton Trans.* **1997**, 415.
[48] R. Usón, J. Laguna, J. Vicente, *J. Organomet. Chem.* **1977**, *131*, 471.
[49] J. Vicente, M. T. Chicote, P. González-Herrero, P. G. Jones, *Inorg. Chem.* **1997**, *36*, 5735.
[50] J. M. Bobbitt, Z. Ma, Q. Huang, *J. Org. Chem.* **1993**, *58*, 4837.

Received: June 30, 2000 [F2579]

0947-6539/01/0703-0646 $ 17.50+.50/0