

## Gold(I) and Palladium(II) Complexes Containing the Functionalized Ylides Triarylphosphonium Cyanomethylide or 2-Cyanoethylide ( $R_3P=CHR'$ , $R' = CN, CH_2CN$ )

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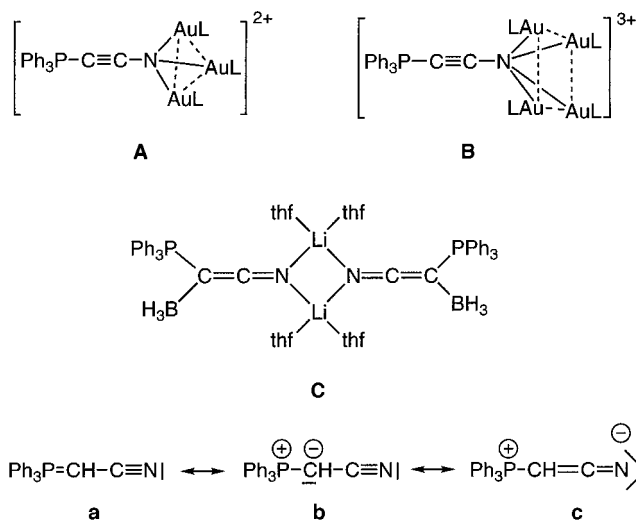
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The coordination properties of ylides  $R_3P=CHCN$  and  $R_3P=CHCH_2CN$  were studied. Ylide  $R_3P=CHCN$  reacts with  $[AuCl(tht)]$  (molar ratio 1:1, tht = tetrahydrothiophene) to give  $[AuCl\{CH(PPh_3)CN\}]$  (**1**). Dinuclear complexes  $[(AuL)_2\{\mu-C(PR_3)CN\}]ClO_4 \cdot nH_2O$  ( $n = 1, L = PPh_3, R = Ph$  (**2a**) or  $Tol (= 4-MeC_6H_4)$  (**2b**);  $n = 0, R = Tol, L = P(pmp)_3$  (**2c**;  $pmp = 4-MeOC_6H_4$  or  $AsPh_3$  (**2d**)) are the products of reactions between phosphonium salts  $(R_3PCH_2CN)ClO_4$  ( $R = Ph$  or  $Tol$ ) and  $[Au(acac)L]$  (molar ratio 1:3,  $L = PPh_3$  or  $P(pmp)_3$ ;  $acacH = acetylacetone$ ). The reaction of  $[Au(acac)PPh_3]$  with  $(Ph_3PCH_2CH_2CN)ClO_4$  ( $Au/P$  2–5) gives the mononuclear complex  $[Au\{CH(PPh_3)CH_2CN\}(PPh_3)]ClO_4 \cdot 0.5H_2O$  (**3**). Complexes **2b** or **2c** react with  $[Au(acetone)L]ClO_4$  (molar ratio 1:1,  $L = PPh_3$  or  $P(pmp)_3$ ), prepared *in situ* from  $[AuCl(L)]$  and  $AgClO_4$  in acetone, to give the corresponding trinuclear derivatives  $[(AuL)_2\{\mu_3-C(PTol_3)CN\}(AuL)](ClO_4)_2$  ( $L = PPh_3$  (**4a**) or  $P(pmp)_3$  (**4b**)). We attempted unsuccessfully to prepare single crystals of **4a** or **4b** or of the triflate salt  $[\{Au(PPh_3)_2\}\{\mu_3-C(PTol_3)CN\}(AuPPh_3)](TfO)_2 \cdot H_2O$  (**4a'**), obtained by reacting **4a** with 2 equiv. of  $KCF_3SO_3$ . In complexes **2** and **4**, two new types of coordination of the ylides  $R_3P=CHCN$  are present. Attempts to coordinate three  $AuL$  groups to the N-atom of  $(R_3PCCN)^-$  induced by aurophilicity (see **A** and **B**) were unsuccessful. The reaction between  $PdCl_2$  and  $R_3P=CHCN$  (molar ratio 1:2) gives *trans*- $[PdCl_2\{CH(PTol_3)CN\}_2]$  (**5**).

**Introduction.** – We have previously reported the synthesis of gold [1–9], silver [6–12], and palladium [13–15] complexes containing phosphorus ylides as ligands. Most of these ylides were carbonyl-stabilized  $R_3P=CHC(O)R'$  ( $R = Ph$  or  $Tol (= 4-MeC_6H_4)$ ,  $R' = Me, Ph, MeO, EtO, \text{ or } Me_2N$ ) and, in spite of their weak nucleophilic character, gave stable and interesting complexes. In this paper, we describe gold(I) and palladium(II) complexes of the cyano-stabilized ylide  $R_3P=CHCN$  (triarylphosphonium cyanomethylide). Very few complexes of this ligand are known [8][16–20]: We have reported the only gold complex,  $[\{Au(PPh_3)_2\}\{\mu-C(PTol_3)CN\}]$  ( $L = PPh_3$ ) [8]. We were interested in using this ligand because of the tendency of  $Au^I$  complexes to aggregate through weak  $Au \cdots Au$  bonds. Such aurophilic interactions are responsible for the synthesis of very interesting compounds containing hypercoordinated C-, N-, or P-atoms [21–25]. With these precedents in mind, we reasoned that, after deprotonation,  $R_3P=CHCN$  could give tri- or tetranuclear gold(I) complexes **A** or **B**.

The ligand  $R_3P=CHCN$  is a stabilized phosphorus ylide due to the fact that, in addition to the ylene and ylide resonance forms **a** and **b**, respectively, common to all phosphorus ylides, the resonance form **c** contributes a certain electronic delocalization.

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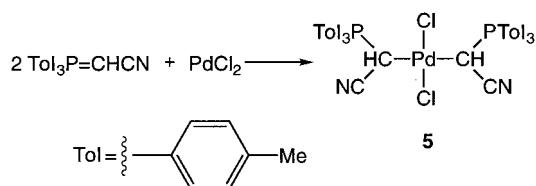
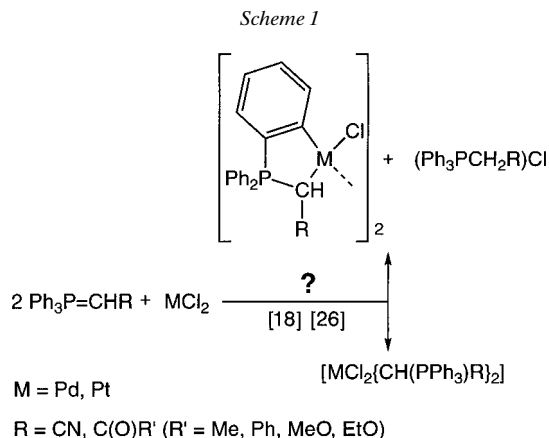


The ability of the N-atom to withdraw electron density from the methine C-atom is shown by the existence of complex **C** in which the methine proton of  $\text{R}_3\text{P}=\text{CHCN}$  has been substituted by  $\text{BH}_3$  and the N-atom bridges two  $\text{Li}(\text{thf})_2$  units [20]. This makes  $\text{R}_3\text{P}=\text{CHCN}$  an interesting ambidentate ligand. *Navarro* and coworkers have synthesized complexes in which this ligand is N- or C-coordinated or bridging N- and C-coordinated [16][17].

In this paper, we also describe the synthesis of the complex  $[\text{PdCl}_2\{\text{CH}(\text{PR}_3)\text{CN}\}_2]$  ( $\text{R} = \text{Tol}$ ). An analogue to this complex ( $\text{R} = \text{Ph}$ ) and a family of Pd and Pt complexes with carbonyl-stabilized ligands were previously reported [18], but later shown to be mixtures of phosphonium salts and *ortho*-metallated complexes (*Scheme 1*) [13][26][27].

**Results.** – The reaction between the ylide  $\text{Ph}_3\text{P}=\text{CHCN}$  and  $[\text{AuCl}(\text{tht})]$  (molar ratio 1:1, 1 h, room temperature,  $\text{CH}_2\text{Cl}_2$ ; tht = tetrahydrothiophene) gave  $[\text{AuCl}\{\text{CH}(\text{PPh}_3)\text{CN}\}]$  (**1**) (*Scheme 2*). Acid-base reactions of phosphonium salts  $(\text{R}_3\text{PCH}_2\text{CN})\text{ClO}_4$  ( $\text{R} = \text{Ph}$ , Tol) with  $[\text{Au}(\text{acac})\text{L}]$  (molar ratio 1:3,  $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{pmp})_3$  ( $\text{pmp} = 4\text{-MeOC}_6\text{H}_4$ );  $\text{acacH} = \text{acetylaceton}$ ) gave dinuclear complexes  $[(\text{AuL})_2\{\mu\text{-C}(\text{PR}_3)\text{CN}\}]\text{ClO}_4 \cdot n\text{H}_2\text{O}$  ( $n = 1$ ,  $\text{L} = \text{PPh}_3$ ,  $\text{R} = \text{Ph}$  (**2a**) or Tol (**2b**) [8];  $n = 0$ ,  $\text{R} = \text{Tol}$ ,  $\text{L} = \text{P}(\text{pmp})_3$  (**2c**) or  $\text{AsPh}_3$  (**2d**)) (*Scheme 2*) which are unprecedented metal derivatives of cyano-stabilized ylides. The substitution of more than one methylene H-atom of  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{ClO}_4$  by a metallic moiety was not achieved. Thus, reactions of  $[\text{Au}(\text{acac})(\text{PPh}_3)]$  with different amounts of  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{ClO}_4$  ( $\text{Au/P}$  2–5) always gave the mononuclear complex  $[\text{Au}\{\text{CH}(\text{PPh}_3)\text{CH}_2\text{CN}\}(\text{PPh}_3)]\text{-ClO}_4 \cdot 0.5\text{H}_2\text{O}$  (**3**).

Several attempts to prepare N-coordinated derivatives of complexes **2** and **3** were carried out with different results. Thus, while neither one reacted with  $\text{AgClO}_4$  in a 1:1 (**2b**, **3**) or 2:1 (**2b**) molar ratio, **2b** or **2c** reacted with  $[\text{Au}(\text{acetone})\text{L}]\text{ClO}_4$  (molar ratio 1:1,  $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{pmp})_3$ ), prepared *in situ* from  $[\text{AuClL}]$  and  $\text{AgClO}_4$  in acetone, to



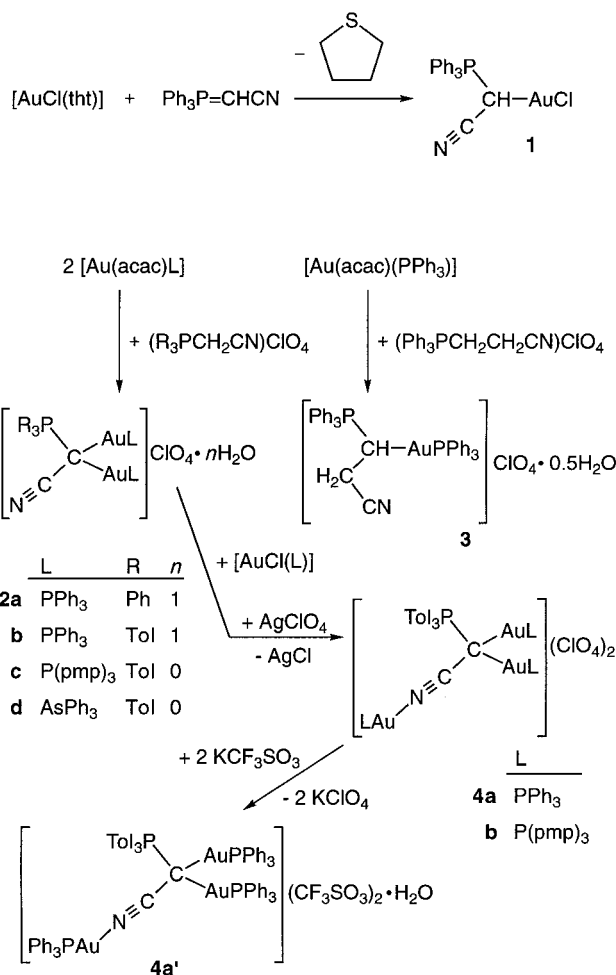
give the corresponding trinuclear derivatives  $[(\text{AuL})_2\{\mu_3\text{-C}(\text{PTol}_3)\text{CN}\}(\text{AuL})]\text{-}(\text{ClO}_4)_2$  ( $\text{L} = \text{PPh}_3$  (**4a**) or  $\text{P}(\text{pmp})_3$  (**4b**)). Complex **3** led to decomposition products under the same reaction conditions. We attempted unsuccessfully to grow single crystals of **4a** or **4b** or of the triflate salt  $[(\text{Au}(\text{PPh}_3))_2\{\mu_3\text{-C}(\text{PTol}_3)\text{CN}\}\{\text{Au}(\text{PPh}_3)\}]\text{-}(\text{TfO})_2 \cdot \text{H}_2\text{O}$  (**4a'**), obtained by reacting **4a** with 2 equiv. of  $\text{K}(\text{CF}_3\text{SO}_3)$ . Complexes **4** are also unprecedented metal derivatives of cyano-stabilized ylides.

Attempts to coordinate three  $\text{AuL}$  groups to the N-atom of  $(\text{R}_3\text{P}=\text{CCN})^-$  induced by aurophilicity (see **A** and **B**) were unsuccessful. Thus, a 1:1 mixture of **2c** and triphos ( $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ) led to the recovery of the starting materials, while the reaction of **2d** with triphos and  $[\text{AuCl}(\text{tht})]$  (molar ratio 1:1:1) gave an unresolvable mixture. The same occurred when  $[(\text{AuCl})_3(\text{triphos})]$  was reacted with  $[\text{Tl}(\text{acac})]$  and  $(\text{Tol}_3\text{-PCH}_2\text{CN})\text{ClO}_4$  (molar ratio 1:2:1), or when **2d** was reacted with  $[\text{Au}(\text{acetone})\text{-}(\text{AsPh}_3)]\text{ClO}_4$  and triphos (molar ratio 1:1:1).

The reaction between  $\text{PdCl}_2$  and  $\text{R}_3\text{P}=\text{CHCN}$  (molar ratio 1:2, 2 h refluxing in acetone) gave *trans*- $[\text{PdCl}_2\{\text{CH}(\text{PTol}_3)\text{CN}\}_2]$  (**5**) (*Scheme 1*).

**Discussion.** – In spite of its low nucleophilicity,  $\text{Ph}_3\text{P}=\text{CHCN}$  is able to substitute the weak donor ligand tetrahydrothiophene (tht) in  $[\text{AuCl}(\text{tht})]$ , to give **1** (*Scheme 2*). In this context, this ylide is comparable to carbonyl-stabilized  $\text{R}_3\text{P}=\text{CHC}(\text{O})\text{R}'$  ( $\text{R} = \text{Ph}$  or  $\text{Tol}$ ;  $\text{R}' = \text{Me, Ph, MeO}$  or  $\text{EtO}$ ) [1][3]. The parallelism can be extended to phosphonium salts  $[\text{R}_3\text{PCH}_2\text{C}(\text{O})\text{R}']^+$  and  $(\text{R}_3\text{PCH}_2\text{CN})^+$ , as both are acidic enough to displace the weak acid acetylacetone from  $[\text{Au}(\text{acac})\text{L}]$  to give dinuclear complexes, *e.g.*,

Scheme 2



**2a–d.** However, there is an important difference. While  $[\text{R}_3\text{PCH}_2\text{C}(\text{O})\text{R}]^+$  salts react with  $[\text{Au}(\text{acac})\text{L}]$  in 1 : 1 molar ratios to give mononuclear complexes  $[\text{Au}\{\text{CH}(\text{PR}_3)\text{C}(\text{O})\text{R}\}\text{L}]$ , the result of reacting  $[\text{Au}(\text{acac})(\text{PPh}_3)]$  and  $(\text{Ph}_3\text{PCH}_2\text{CN})\text{ClO}_4$  in an 1 : 1 molar ratio is an irresolvable mixture containing (deduced by NMR spectroscopy) the dinuclear complex **2a**, the phosphonium salt, and the expected mononuclear derivative  $[\text{Au}\{\text{CH}(\text{PPh}_3)\text{CN}\}(\text{PPh}_3)]\text{ClO}_4$ . A similar reactivity towards  $[\text{Au}(\text{acac})(\text{PPh}_3)]$  has been reported for the non-stabilized phosphonium salt  $[\text{Ph}_3\text{PCH}_2(\text{py}-2)]\text{ClO}_4$  ( $\text{py}-2 = 2\text{-pyridyl}$ ) [9]. In this case, we have established that the monosubstituted complex  $[\text{Au}\{\text{CH}(\text{PPh}_3)(\text{py}-2)\}(\text{PPh}_3)]$  is in equilibrium with the phosphonium salt and the dinuclear species  $[\{\text{Au}(\text{PPh}_3)\}_2\{\mu\text{-C}(\text{PPh}_3)(\text{py}-2)\}]$  since the same mixture of three products (phosphonium salt and mononuclear and dinuclear complex) was obtained when  $[\text{AuCl}\{\text{CH}(\text{PPh}_3)(\text{py}-2)\}]$  was reacted

with  $\text{AgClO}_4$  (molar ratio 1:1) and, after removal of  $\text{AgCl}$ , 1 equiv. of  $\text{PPh}_3$  was added.

The phosphonium salt  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{ClO}_4$  is less acidic than  $(\text{Ph}_3\text{PCH}_2\text{CN})\text{ClO}_4$  because substitution of more than one methylene H-atom was not achieved. Thus, reaction of  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{ClO}_4$  with an excess of  $[\text{Au}(\text{acac})(\text{PPh}_3)]$  (Au/P 2–5) gave the mononuclear complex  $[\text{Au}\{\text{CH}(\text{PPh}_3)\text{CH}_2\text{CN}\}(\text{PPh}_3)]\text{ClO}_4 \cdot 0.5 \text{H}_2\text{O}$  (**3**), while the reaction in a 1:1 molar ratio led to a mixture of **3** and the starting materials. Such decreasing acidity is a consequence of the reduction of the inductive effect of both  $\text{Ph}_3\text{P}$  and  $\text{CN}$  groups with increasing distance. We were also unable to synthesize silver derivatives of this phosphonium salt by reacting it with basic silver salts; the reaction of  $\text{Ag}_2\text{CO}_3$  with  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{Cl}$  and  $\text{AgClO}_4$  (molar ratio 1:1:1) at room temperature or refluxing in acetone gave  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{ClO}_4$ ,  $\text{AgCl}$ , and unreacted  $\text{Ag}_2\text{CO}_3$ . This method has been applied successfully in the preparation of ylide complexes of silver starting from more acidic phosphonium salts, like  $[\text{Ph}_2\text{P}(\text{CH}_2\text{CO}_2\text{R})_2]^+$  ( $\text{R} = \text{Me}, \text{Et}$ ) [11]. The use of a stronger base such as  $\text{NaH}$  also did not result in the formation of the desired complexes. Thus, the reaction between  $(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CN})\text{Cl}$  and  $\text{NaH}$  in the presence of  $\text{AgClO}_4$  gave a complicated mixture of compounds from which only the decomposition product  $\text{Ph}_3\text{PO}$  was identified.

Because we were interested in using the ligands  $(\text{R}_3\text{PCCN})^-$  in the chemistry of gold(I) for the tendency of the latter to form weak  $\text{Au} \cdots \text{Au}$  bonds, thus inducing possibly aggregation of three or four  $\text{AuPR}_3$  groups around the N-atom (see above, **A** or **B**), several attempts to prepare N-coordinated derivatives of complexes **2** and **3** were carried out. However, while **2b** or **2c** reacted with  $[\text{Au}(\text{acetone})\text{L}]\text{ClO}_4$  ( $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{pmp})_3$ ) to give the corresponding trinuclear derivatives  $[(\text{AuL})_2\{\mu_3\text{-}\{\text{C}(\text{PTol}_3)\text{-CN}\}(\text{AuL})\}](\text{ClO}_4)_2$  ( $\text{L} = \text{PPh}_3$  (**4a**) or  $\text{P}(\text{pmp})_3$  (**4b**)) containing only one  $\text{AuL}$  group bonded to N, complex **3** led to decomposition products under the same reaction conditions.

The formation of  $[\text{PdCl}_2\{\text{CH}(\text{PTol}_3)\text{CN}\}_2]$  (**5**) from  $\text{PdCl}_2$  and  $\text{ToI}_3\text{P}=\text{CHCN}$  in refluxing acetone (*Scheme 1*) can be compared to the formation of similar complexes initially formulated as  $[\text{MCl}_2\{\text{CH}(\text{PPh}_3)\text{R}'\}_2]$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ;  $\text{R}' = \text{C}(\text{O})\text{R}'$  ( $\text{R}' = \text{Me}, \text{Ph}, \text{EtO}$  or  $\text{MeO}$ )) which were proposed to result from reacting  $\text{MCl}_2$  with the corresponding ylide in hot  $\text{MeCN}$  [18]. However, some of these complexes with carbonyl-stabilized ylides were later shown to be mixtures of the *ortho*-metallated complexes  $[\text{M}\{\text{CH}\{\text{P}(2\text{-C}_6\text{H}_4)\text{Ph}_2\}\{\text{C}(\text{O})\text{R}'\}\}(\mu\text{-Cl})]_2$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ;  $\text{R}' = \text{Me}, \text{Ph},$  or  $\text{MeO}$ ) and the corresponding phosphonium salt  $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{R}]\text{Cl}$  (*Scheme 1*) [13][26][27]. We have already studied the reactivity of  $\text{PdCl}_2$  towards the ylide  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$  [13]: the room-temperature reaction (1:2 molar ratio) in  $\text{MeCN}$  gave  $[\text{PdCl}_2\{\text{CH}(\text{PPh}_3)\text{CO}_2\text{Me}\}_2]$  which evolved to the *ortho*-metallated compound  $[\text{Pd}\{\text{CH}\{\text{P}(2\text{-C}_6\text{H}_4)\text{Ph}_2\}\text{CO}_2\text{Me}\}(\mu\text{-Cl})]_2$  and the phosphonium salt when refluxed, whereas the reaction (1:1 molar ratio) in boiling  $\text{MeCN}$  gave only the *ortho*-metallated complex. Similarly,  $\text{ToI}_3\text{P}=\text{CHCN}$  and  $\text{PdCl}_2$  (2:1 molar ratio) in refluxing acetone gave **5** after 2 h (*Scheme 1*) while a mixture of **5**, the phosphonium salt and the *ortho*-metallated compound could be detected by NMR spectroscopy after 20 h. Although some other  $[\text{PdX}_2\{\text{CH}(\text{PR}_3)\text{R}'\}_2]$  complexes with  $\text{R}' = \text{C}(\text{O})\text{R}''$  have been isolated [28][29], the reaction of  $\text{PdCl}_2$  with ylides  $\text{R}_3\text{P}=\text{CHCN}$  had never been reinvestigated.

The product previously reported [18] and formulated as  $[\text{PdCl}_2\{\text{CH}(\text{PPh}_3)\text{CN}\}_2]$ , *i. e.* **5** with Ph instead of Tol, was characterized by elemental analyses and IR spectroscopy; we believe that the isolated product was in fact a mixture of the phosphonium salt and the *ortho*-metallated complex (see below).

**Structure of Complexes.** – The NMR spectra of complexes **1** and **5** show that the coordination of  $\text{R}_3\text{P}=\text{CHCN}$  is through the methine C-atom. Thus, the coupling constant  $^1J(\text{P,C})$  of the C-atom in  $\alpha$ -position to the CN group has similar values in complexes **1** (52.8 Hz) and **5** (50 Hz), in  $(\text{ToI}_3\text{PCH}_2\text{CN})\text{ClO}_4$  (57.4 Hz), and in other complexes containing this C-bonded ligand (46 Hz) [16], all displaying a  $\text{sp}^3$  hybridization at the C-atom. These  $^1J(\text{P,C})$  values are significantly smaller than those of the  $\text{sp}^2$  CH C-atom in  $\text{ToI}_3\text{P}=\text{CHCN}$  (135.5 Hz) or in complexes containing this ligand coordinated through the N-atom (137–135 Hz) [16]. The  $^1\text{H-NMR}$  spectra of complexes **1** and **5** show  $\delta(\text{H})$  and  $^2J(\text{HP})$  values for  $\text{CH}(\alpha)$  (**1**: 3.74 ppm, 12 Hz; **5**: 3.62, 3.70 ppm, 13 Hz) in the ranges observed for Pd complexes containing this C-bonded ylide ligand (4.58–3.05 ppm, 14–13 Hz) and far from the values in complexes containing the N-bonded ylide ligand (2.03–1.06 ppm, 6–5 Hz) [16][17]. The  $\delta(\text{C})$  and  $\delta(\text{P})$  values of the P–CH moiety are inconclusive. Some resonances in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, as well as that expected in the  $^{31}\text{P}$ -NMR spectrum of **5**, are duplicated, as anticipated for a molecule containing two chiral centers (*Scheme 1*).

The proposed structure for complexes **2a–d**, in which two AuL groups are bonded to the C( $\alpha$ ) atom, is based on the lack of the CH resonance in their  $^1\text{H-NMR}$  spectra, the observation of only two resonances in the  $^{31}\text{P-NMR}$  spectra of **2a–c**, and on the crystal structures of related complexes [1][2][6–8]. In addition, the preference of Au<sup>I</sup> for C- with respect to N-donor ligands makes the proposed structure more plausible than the alternative one, in which both AuL groups are bonded to the N-atom. Moreover, the  $\tilde{\nu}(\text{CN})$  value (2167 (**2a**), 2158 (**2b**), 2164 (**2c**), 2157 (**2d**)  $\text{cm}^{-1}$ ) is similar to that observed in the other complexes with the C-bonded ylide (2202 (**1**), 2183 (**5**)  $\text{cm}^{-1}$ ). A marked decrease in the  $\nu(\text{CN})$  frequency should be observed if coordination had taken place through the N-atom.

Complex **3** does not show any band in its IR spectrum between 2000–2300  $\text{cm}^{-1}$  assignable to a  $\tilde{\nu}(\text{CN})$  vibration mode. The corresponding phosphonium salts show a very weak band at 2239  $\text{cm}^{-1}$ . The  $^{13}\text{C}$ - and  $^{13}\text{C-DEPT-NMR}$  spectra of complex **3** allowed us to distinguish between the isomers  $[\text{Au}\{\text{CH}(\text{PPh}_3)\text{CH}_2\text{CN}\}(\text{PPh}_3)]$  and  $[\text{Au}\{\text{CH}(\text{CN})\text{CH}_2\text{PPh}_3\}(\text{PPh}_3)]$ . Thus, the C-atom of the CH moiety is coupled with two different P-nuclei with coupling constants ( $^1J=83$  and  $^2J=38$  Hz) that are significantly greater than those of the  $\text{CH}_2$  group ( $^2J=4$  and  $^3J=2.5$  Hz), which is consistent with coordination of the  $\text{Ph}_3\text{PAu}$  group to the ylide C( $\alpha$ ) atom.

When the IR spectra of trinuclear complexes **4a** and **4b** are compared with those of the parent dinuclear complexes **2b** and **2c**, no significant variation in the  $\tilde{\nu}(\text{CN})$  band is observed upon coordination of the third metal center. The  $^{31}\text{P-NMR}$  spectra of complexes **4a** and **4b** are in accord with the proposed structures. However, the broadening of the  $\text{Ph}_3\text{PAuN}$  resonance in **4a** and of the three resonances in **4b** show that exchange processes occur in solution at room temperature. A  $^1\text{H}$ - and  $^{31}\text{P}$  NMR spectroscopic study of **4b** in the range of +60 to –55° shows that at least two different species are present in solution at low temperatures. However, it is difficult to elucidate

their structures. The IR spectrum of complex **1** shows one  $\tilde{\nu}(\text{AuCl})$  band at  $325\text{ cm}^{-1}$  which lies in the normal range of  $310\text{--}340\text{ cm}^{-1}$  found in similar complexes where coordination to the C-atom is well established [1–3][6]. Complex **5** shows one  $\tilde{\nu}(\text{PdCl})$  band at  $321\text{ cm}^{-1}$ , consistent with a *trans* configuration [29]. This is also the geometry found in the complex  $[\text{PdCl}_2\{\text{CH}(\text{PBu}_3)\text{C}(\text{O})\text{Ph}\}_2]$  [30].

The IR spectrum of complex **1** shows the  $\tilde{\nu}(\text{CN})$  band at  $2202\text{ cm}^{-1}$ ,  $67\text{ cm}^{-1}$  higher and  $33\text{ cm}^{-1}$  lower than that of the ylide  $\text{Ph}_3\text{P}=\text{CHCN}$  and the phosphonium salt  $(\text{Ph}_3\text{PCH}_2\text{CN})\text{ClO}_4$ , respectively. The same sequence  $\tilde{\nu}(\text{CN})_{\text{ylide}} < \tilde{\nu}(\text{CN})_{\text{complex}} < \tilde{\nu}(\text{CN})_{\text{phosphonium salt}}$ , is observed for complex **5** ( $\tilde{\nu}(\text{CN})$   $2183\text{ cm}^{-1}$ ), the ylide  $\text{ToI}_3\text{P}=\text{CHCN}$  ( $\tilde{\nu}(\text{CN})$   $2142\text{ cm}^{-1}$ ), and the phosphonium salt  $(\text{ToI}_3\text{PCH}_2\text{CN})\text{ClO}_4$  ( $\tilde{\nu}(\text{CN})$   $2257\text{ cm}^{-1}$ ). The product of the reaction between  $\text{PdCl}_2$  and  $\text{Ph}_3\text{P}=\text{CHCN}$  in refluxing  $\text{MeCN}$ , *i.e.*  $[\text{PdCl}_2\{\text{CH}(\text{PPh}_3)\text{CN}\}_2]$  (see **5**, with Ph instead of Tol) was reported to give two bands at  $2248$  and  $2189\text{ cm}^{-1}$  instead of only one. The presence of the one at higher frequency suggests it was a mixture containing the phosphonium salt and an *ortho*-palladated complex (*Scheme 1*) [18].

The contribution of resonance form **c** (see above) to the electronic distribution in the  $\text{R}_3\text{P}=\text{CHCN}$  ylides, but not in their complexes or in the phosphonium salts, justifies the lowest values for  $\tilde{\nu}(\text{CN})_{\text{ylide}}$ . If complexes are considered as metallated phosphonium salts, the lower electronegativity of the groups  $\text{AuCl}$  or  $\text{PdCl}_2$  (ylide) compared to the H-atom accounts for the highest values for  $\tilde{\nu}(\text{CN})_{\text{phosphonium salt}}$ . In accord with this argument, substitution of both H-atoms in phosphonium salts by AuL groups lead to  $\tilde{\nu}(\text{CN})$  values ( $2167\text{--}2157\text{ cm}^{-1}$  in complexes **2a–d**) lower than that observed in the mononuclear complex **1**. The same relationships have been found for the  $\tilde{\nu}(\text{CO})$  band in carbonyl-stabilized phosphorus ylide complexes with respect to the corresponding ylides and phosphonium salts [3]. Coordination of a third group to the N-atom, as in complexes **4** ( $2164\text{ cm}^{-1}$ ), do not change  $\tilde{\nu}(\text{CN})$  values with respect to those of complexes **2a–d**. It is well known that  $\text{N}_\sigma$ -coordination of nitriles can cause the  $\tilde{\nu}(\text{CN})$  to shift to either higher, lower, or similar frequency with respect to that of the free nitrile [31].

### Experimental Part

*General.* Complex  $[\{\text{Au}(\text{PPh}_3)\}_2\{\mu\text{-C}(\text{PTol}_3)\text{CN}\}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  (**2b**) has been described previously [8]. The C, H, and N analyses, conductance measurements, IR spectra (in  $\text{cm}^{-1}$ ) and melting-point determinations were carried out as described elsewhere [32]. NMR Spectra: *Varian-Unity-300* spectrometer; in  $\text{CDCl}_3$  at r.t., unless stated otherwise;  $\delta$  in ppm rel. to  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}\{^1\text{H}\}$ ) *J* in Hz.

*Chloro[cyano(triphenylphosphonio)methyl]gold*  $[\text{AuCl}\{\text{CH}(\text{PPh}_3)\text{CN}\}]$ ; (**1**).  $[\text{AuCl}(\text{tht})]$  ( $148.2\text{ mg}$ ,  $0.462\text{ mmol}$ ) was added to a soln. of triphenylphosphonium cyanomethylide (= (triphenylphosphoranyl-ylidene)acetonitrile;  $\text{Ph}_3\text{P}=\text{CHCN}$ ;  $139.3\text{ mg}$ ,  $0.462\text{ mmol}$ ) in  $\text{CH}_2\text{Cl}_2$  ( $20\text{ ml}$ ). After 1 h, the soln. was concentrated to *ca.*  $2\text{--}3\text{ ml}$  and filtered through anhyd.  $\text{MgSO}_4$ . The filtrate was added to  $\text{Et}_2\text{O}$  ( $30\text{ ml}$ ), the suspension concentrated to *ca.* half of its volume, and *n*-hexane ( $10\text{ ml}$ ) added to give **1** as a white solid, which was filtered and air dried. Yield 78%. M.p.  $185^\circ$  (dec.).  $A_M$  ( $\Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ ) = 0. IR:  $2202$  (CN),  $325$  (AuCl).  $^1\text{H-NMR}$ :  $3.74$  (*d*,  $^2J(\text{P,H}) = 12$ , CH);  $7.6\text{--}7.9$  (*m*, 3 Ph).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ :  $2.4$  (*d*,  $^1J(\text{P,C}) = 52.8$ , CH);  $118.5$  (*d*,  $^2J(\text{P,C}) = 6.5$ , CN);  $121.5$  (*d*,  $^1J(\text{P,C}) = 89$ ,  $C_{\text{ipso}}$ );  $130.1$  (*d*,  $^3J(\text{P,C}) = 12.6$ ,  $C_m$ );  $133.5$  (*d*,  $^2J(\text{P,C}) = 9.5$ ,  $C_o$ ),  $134.7$  (*d*,  $^4J(\text{P,C}) = 3.4$ ,  $C_p$ ).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ :  $25.70$  (*s*). Anal. calc. for  $\text{C}_{20}\text{H}_{16}\text{AuClNP}$ : C 45.01, H 3.02, N 2.62, Au 36.90; found: C 44.62, H 3.31, N 2.70, Au 37.20.

$[\mu\text{-}[\text{Cyano}(\text{triphenylphosphonio})\text{methylene}]]\text{bis}(\text{triphenylphosphine})\text{digold}(1+)$  Perchlorate Hydrate ( $1:1:1$ ) ( $[\{\text{Au}(\text{PPh}_3)\}_2\{\mu\text{-C}(\text{PPh}_3)\text{CN}\}]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ; **2a**) and  $[\mu\text{-}[\text{Cyano}[\text{tris}(4\text{-methylphenyl})\text{phosphonio}]\text{methylene}]]\text{bis}[\text{tris}(4\text{-methoxyphenyl})\text{phosphine}]\text{digold}(1+)$  Perchlorate ( $[\{\text{Au}(\text{pmp})\}_2\{\mu\text{-C}(\text{PTol}_3)\text{CN}\}]\text{ClO}_4$ ; **2c**).  $[\text{Au}(\text{acac})\text{L}]$  ( $\text{L} = \text{PPh}_3$ ,  $217.2\text{ mg}$ ,  $0.389\text{ mmol}$ ;  $\text{L} = \text{P}(\text{pmp})_3$ ,  $469.2\text{ mg}$ ,  $0.723\text{ mmol}$ ) was added to a soln. of

(cyanomethyl)triphenyl- or (cyanomethyl)tris(4-methylphenyl)phosphonium perchlorate ((R<sub>3</sub>PCH<sub>2</sub>CN)ClO<sub>4</sub>; R = Ph, 52.2 mg, 0.129 mmol; R = Tol, 109.2 mg, 0.246 mmol) in acetone (20 ml). The resulting suspension was stirred (R = Ph, 19 h; R = Tol, 72 h), and filtered through anh. MgSO<sub>4</sub>. The filtrate was concentrated to ca. 2 ml and Et<sub>2</sub>O (20 ml) added to precipitate **2a** or **2c** as a white solid, which was filtered, washed with Et<sub>2</sub>O, and air-dried.

*Data of 2a:* Yield 93%. M.p. 169° (dec.).  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 124. IR: 2167 (CN). <sup>1</sup>H-NMR: 1.68 (s, 2H, H<sub>2</sub>O); 7.1–7.9 (m, 9 Ph). <sup>31</sup>P{<sup>1</sup>H}-NMR: 33.51 (s, Ph<sub>3</sub>PC); 36.93 (s, Ph<sub>3</sub>PAu). Anal. calc. for C<sub>56</sub>H<sub>47</sub>Au<sub>2</sub>ClNO<sub>3</sub>P<sub>3</sub>: C 50.33, H 3.54, N 1.05, Au 29.48. Found: C 50.10, H 3.84, N 1.14, Au 29.42.

*Data of 2c:* Yield 95%. M.p. 242° (dec.).  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 132. IR: 2164 (CN). <sup>1</sup>H-NMR: 2.44 (s, 3 Me); 3.83 (s, 6 MeO); 6.79 (dd, <sup>3</sup>J(H,H) = 8, <sup>4</sup>J(P,H) = 1, 12 H, MeOC<sub>6</sub>H<sub>4</sub>); 7.11 (dd, <sup>3</sup>J(P,H) = 12, 12 H, MeOC<sub>6</sub>H<sub>4</sub>); 7.24 (dd, <sup>3</sup>J(H,H) = 8, <sup>4</sup>J(P,H) = 2, 6 H, MeC<sub>6</sub>H<sub>4</sub>); 7.74 (dd, <sup>3</sup>J(P,H) = 12, 6 H, MeC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR: 32.40 (t, <sup>3</sup>J(P,P) = 6, Tol<sub>3</sub>PC); 32.92 (d, (pmp)<sub>3</sub>PAu). Anal. calc. for C<sub>65</sub>H<sub>63</sub>Au<sub>2</sub>ClNO<sub>10</sub>P<sub>3</sub>: C 50.68, H 4.12, N 0.91; found: C 50.60, H 4.42, N 0.97.

{μ-[Cyanotris(4-methylphenyl)phosphonio]methylene}bis(triphenylarsine)digold(I+) Perchlorate ([Au(AsPh<sub>3</sub>)<sub>2</sub>]{μ-C(PTol<sub>3</sub>CN)}]ClO<sub>4</sub>; **2d**). [Au(acac)(AsPh<sub>3</sub>)<sub>2</sub>] (429.6 mg, 0.713 mmol) was added to a soln. of (cyanomethyl)tri(4-tolyl)phosphonium perchlorate ((Tol<sub>3</sub>PCH<sub>2</sub>CN)ClO<sub>4</sub>; 79.1 mg, 0.178 mmol) in acetone (30 ml). The resulting suspension was stirred under N<sub>2</sub> for 3 h and filtered through *Celite*. The filtrate was concentrated to ca. 2 ml and Et<sub>2</sub>O added (20 ml) to precipitate **2d** as an off-white solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Yield 62%. M.p. 134° (dec.).  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 127. IR: 2157 (CN). <sup>1</sup>H-NMR: 2.43 (s, 3 Me); 7.2–7.8 (m, 42 H, Tol, Ph). <sup>31</sup>P{<sup>1</sup>H}-NMR: 31.3 (s, Tol<sub>3</sub>PC). Anal. calc. for C<sub>59</sub>H<sub>51</sub>As<sub>2</sub>Au<sub>2</sub>ClNO<sub>4</sub>P: C 48.93, H 3.55, N 0.97; found: C 48.86, H 3.42, N 1.07.

[2-Cyano-1-(triphenylphosphonio)ethyl](triphenylphosphine)gold(I+) Perchlorate Hydrate (2:2:1) ([Au{CH(PPh<sub>3</sub>)CH<sub>2</sub>CN}(PPh<sub>3</sub>)ClO<sub>4</sub>·0.5 H<sub>2</sub>O; **3**) [Au(acac)(PPh<sub>3</sub>)<sub>2</sub>] (211.4 mg, 0.378 mmol) was added to a soln. of (2-cyanoethyl)triphenylphosphonium perchlorate ((Ph<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CN)ClO<sub>4</sub>; 78.7 mg, 0.189 mmol) in acetone (20 ml). The resulting suspension was stirred under N<sub>2</sub> for 29 h and then filtered through anh. MgSO<sub>4</sub>. The filtrate was concentrated to 1 ml and Et<sub>2</sub>O (20 ml) added to precipitate **3** as an off-white solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Yield 91%. M.p. 106°.  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 124. <sup>1</sup>H-NMR: 1.63 (s, 1 H, H<sub>2</sub>O); 3.09 (m, CH); 3.47 (m, CH<sub>2</sub>); 7.2–7.9 (m, 6 Ph). <sup>13</sup>C-NMR: 17.63 (dd, <sup>2</sup>J(P,C) = 4, <sup>3</sup>J(P,C) = 2.5, CH<sub>2</sub>); 27.17 (dd, <sup>1</sup>J(P,C) = 83, <sup>2</sup>J(P,C) = 38, CH); 120.1 (dd, <sup>3</sup>J(P,C) = 13, <sup>4</sup>J(P,C) = 2, CN); 122.3 (dd, <sup>1</sup>J(P,C) = 85, <sup>4</sup>J(P,H) = 1.5, C<sub>ipso</sub>); 128.5 (d, <sup>1</sup>J(P,C) = 56, C<sub>ipso</sub>); 129.4 (d, <sup>3</sup>J(P,C) = 11.6, C<sub>m</sub>); 130.2 (d, <sup>3</sup>J(P,C) = 11.6, C<sub>m</sub>); 131.9 (d, <sup>4</sup>J(P,C) = 2.5, C<sub>p</sub>); 133.4 (d, <sup>2</sup>J(P,C) = 9.6, C<sub>o</sub>); 133.9 (d, <sup>2</sup>J(P,C) = 14.1, C<sub>o</sub>); 134.2 (d, <sup>4</sup>J(P,C) = 2.5, C<sub>p</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR: 30.46 (d, J(P,P) = 8, Ph<sub>3</sub>PC); 40.33 (d, Ph<sub>2</sub>PAu). Anal. calc. for C<sub>39</sub>H<sub>34</sub>AuClNO<sub>4.5</sub>P<sub>2</sub>: C 53.05, H 3.88, N 1.58, Au 22.30; found: C 52.88, H 3.75, N 1.55, Au 22.25.

{μ<sub>3</sub>-[(Cyanone-KN)tris(4-methylphenyl)phosphonio]methylene-KC:KC}tris(triphenylphosphine)trigold-(2+) Diperchlorate ([Au(PPh<sub>3</sub>)<sub>2</sub>]{μ<sub>3</sub>-[C(PTol<sub>3</sub>CN)]{Au(PPh<sub>3</sub>)}}](ClO<sub>4</sub>)<sub>2</sub>; **4a**) and {μ<sub>3</sub>-[(Cyanone-KN)tris(4-methylphenyl)phosphonio]methylene-KC:XC}tris(4-methoxyphenyl)phosphine trigold(2+) Diperchlorate ([Au(pmp)<sub>3</sub>]<sub>2</sub>{μ<sub>3</sub>-[C(PTol<sub>3</sub>CN)]{Au(pmp)<sub>3</sub>}}](ClO<sub>4</sub>)<sub>2</sub>; **4b**). To a soln. of [AuCl] (L = PPh<sub>3</sub>, 107.8 mg, 0.218 mmol; L = P(pmp)<sub>3</sub>, 45.5 mg, 0.078 mmol) in acetone (10 ml), under N<sub>2</sub>, 1 equiv. of AgClO<sub>4</sub> was added. The suspension was stirred for 5 min and allowed to settle. The mother liquor was then decanted, and a soln. of **2b** [8] (296.6 mg, 0.218 mmol) or **2c** (120 mg, 0.078 mmol) in acetone (10 ml) was added to the residue. The resulting suspension was stirred for 10 min and filtered through *Celite* and the filtrate concentrated to ca. 5 ml. Addition of Et<sub>2</sub>O (30 ml) gave complex **4a** or **4b**, respectively, as a white solid which was filtered, washed with Et<sub>2</sub>O, and air dried.

*Data of 4b:* Yield 81%. M.p. 150°.  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 260. IR: 2164 (CN). <sup>1</sup>H-NMR: 2.42 (s, 3 MeC<sub>6</sub>H<sub>4</sub>); 7.1–7.7 (m, 57 arom. H). <sup>31</sup>P{<sup>1</sup>H}-NMR: 28.53 (br. s, Ph<sub>3</sub>PAuN); 31.82 (t, J(P,P) = 6.8, Tol<sub>3</sub>PC); 36.28 (d, Ph<sub>3</sub>PAuC). Anal. calc. for C<sub>77</sub>H<sub>66</sub>Au<sub>3</sub>Cl<sub>2</sub>NO<sub>8</sub>P<sub>4</sub>: C 48.19, H 3.47, N 0.73, Au 30.79; found: C 48.23, H 3.70, N 0.74, Au 30.16.

*Data of 4b:* Yield 80%. Mp: 145°.  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 270. IR: 2164 (CN). <sup>1</sup>H-NMR: 2.45 (s, 3 MeC<sub>6</sub>H<sub>4</sub>); 3.84 (s, 6 MeO); 3.85 (s, 3 MeO); 6.8–7.7 (m, 48 arom. H). <sup>31</sup>P{<sup>1</sup>H}-NMR: 24.10 (br. s, (pmp)<sub>3</sub>PAuN); 31.73 (br. s, Tol<sub>3</sub>PC); 32.55 (s, (pmp)<sub>3</sub>PAuC). Anal. calc. for C<sub>86</sub>H<sub>84</sub>Au<sub>3</sub>Cl<sub>2</sub>NO<sub>17</sub>P<sub>4</sub>: C 47.18, H 3.87, N 0.64; found: C 47.36, H 3.92, N 0.76.

{μ<sub>3</sub>-[(Cyano-KN)tris(4-methylphenyl)phosphonio]methylene-XC:KC}tris(triphenylphosphine)trigold-(2+) Bis(trifluoromethanesulfonate) Hydrate (1:1:1) [(AuPPh<sub>3</sub>)<sub>2</sub>{μ-[C(PTol<sub>3</sub>CN)](AuPPh<sub>3</sub>)}](TfO)<sub>2</sub>·H<sub>2</sub>O; **4a'**): KTFo (23.9 mg, 0.127 mmol) was added to a soln. of **4a** (122.2 mg, 0.064 mmol) in acetone (15 ml). The soln. was stirred for 1 h and then evaporated. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and the extract filtered through *Celite*. The filtrate was concentrated to ca. 2 ml and Et<sub>2</sub>O added to give **4a'** as a white solid. Yield 72%. M.p. 125°.  $A_M$  (Ω<sup>-1</sup>·mol<sup>-1</sup>·cm<sup>2</sup>) = 247. IR: 2164 (CN). <sup>1</sup>H-NMR: 1.64 (s, H<sub>2</sub>O); 2.43 (s, 3 MeC<sub>6</sub>H<sub>4</sub>);



7.1–7.7 (*m*, 57 arom. H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR: 28.27 (br. *s*,  $\text{Ph}_3\text{PAuN}$ ); 32.20 (br. *s*,  $\text{ToI}_3\text{PC}$ ); 36.43 (*d*,  $J(\text{P,P}) = 5.3$ ,  $\text{Ph}_3\text{PAuC}$ ). Anal. calc. for  $\text{C}_{75}\text{H}_{68}\text{Au}_3\text{F}_6\text{NO}_7\text{P}_4\text{S}_2$ : C 46.60, H 3.36, N 0.76, S 3.18, Au 29.02; found: C 46.78, H 3.52, N 0.69, S 3.51, Au 31.12.

*trans*-Dichlorobis(cyano[tris(4-methylphenyl)phosphonio]methyl)palladium (*trans*-[ $\text{PdCl}_2\{\text{CH}(\text{PTol}_3)\text{CN}\}_2$ ]; **5**):  $\text{PdCl}_2$  (26.6 mg; 0.150 mmol) was added to a soln. of  $\text{ToI}_3\text{P}=\text{CHCN}$  (103.3 mg, 0.301 mmol) in acetone (15 ml), and the mixture was refluxed for 2 h. The resulting orange suspension was then allowed to cool, stirred at r.t. for 22 h, and filtered. The orange solid was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give **5**. Yield 81%. M.p.  $241^\circ$  (dec).  $A_M$  ( $\Omega^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^2$ ) = 0. IR: 2183 (CN), 321 (PdCl).  $^1\text{H}$ -NMR (both diastereoisomers, in a ca. 1 : 1 ratio): 2.42 (*s*, 3  $\text{MeC}_6\text{H}_4$ ); 3.62, 3.70 (*2d*,  $^2J(\text{P,H}) = 13$ , 1 H, CH); 7.32–7.38 (*m*, 6 arom. H); 7.80–7.90 (*m*, 6 arom. H).  $^{13}\text{C}$  NMR (2 diastereoisomers): –4.3, –5.6 (*2d*,  $^1J(\text{P,C}) = 50$ , CH); 21.7 (*s*, Me); 119.1, 119.4 (*2d*,  $^1J(\text{P,C}) = 90$ ,  $\text{C}_{\text{ipso}}$ ); 122.0, 122.1 (*2d*,  $^2J(\text{P,C}) = 5.8$ , CN); 129.8, 129.9 (*2d*,  $^3J(\text{P,C}) = 13$ ,  $\text{C}_m$ ); 134.4, 134.5 (*2d*,  $^2J(\text{P,C}) = 10$ ,  $\text{C}_o$ ); 144.30, 144.35 (*d*,  $^4J(\text{P,C}) = 2.5$ ,  $\text{C}_p$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (2 diastereoisomers): 25.74 (*s*); 26.76 (*s*). Anal. calc. for  $\text{C}_{46}\text{H}_{44}\text{Cl}_2\text{N}_2\text{PPd}$ : C 63.94, H 5.13, N 3.24; found: C 64.12, H 5.15, N 3.19.

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