An Unusual Bonding Situation in a Novel Au^{I}-Phosphido Complex with a Planar Au_3P_3 Framework

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Dedicated to Professor A. Zschunke on occasion of his 65th birthday

Keywords: Metathesis / Cyclopentadienyl ligands / Chromium / P ligands / Gold

Reaction of the mono-deprotonated derivative of $[\{Cp(CO)_2Mo\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1**) leads to the novel complex $[\{Cp(CO)_2Mo\}_2(\mu\text{-}H)\{\mu_3\text{-}P(H)Au(PPh_3)\}]$ (**2**). In contrast the reaction of the analogous Cr derivative $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1a**) leads under identical conditions to a planar Au_3P_3 cluster $[\{CpCr(CO)_2\}_6(P_3Au_3)]$ (**3**). Both complexes were completely structurally and spectroscopically characterised. Density functional calculations have shown that **3** is characterised by P–Cr–Au multicentre and Cr-P multiple bonding.

Introduction

Polynuclear Au^{I} complexes are a fascinating field of chemistry[1] as there are, for example, planar, wheel-like mixed metal clusters of the type $[M\{Au(mes)\}_5]X$ (M = Cu, Ag; X = PF_6, ClO_4; mes = 2,4,6-trimethylphenyl)[2] and the larger class of chalcogenido-bridged clusters.[3] Among the latter ones are compounds possessing luminescence properties.[4] However, phosphanido (R_2P^-) substituted Au^{I} complexes are rare,[5] and for Au^{I} complexes containing the phosphido (P^{3-}) ligand, only the series of phosphorus-centred homoleptic gold clusters of Schmidbaur et al. exists. These complexes — $P(AuPR_3)_4{}^+$, $P(AuPR_3)_5{}^{2+}$, $P(AuPR_3)_6{}^{3+}$, $(R_3P)_2AuP(AuPR_3)_4{}^{2+}$, $(R_3PAu)_4PAuP(AuPR_3)_4{}^{3+}$ — were synthesized by the reaction of PH_3 or $P(SiMe_3)_3$ and $P_2(SiMe_3)_4$, respectively, with R_3PAu^+.[6] Interestingly, due to their instability no X-ray structural analysis exists so far for the tetrahedrally coordinated phosphido complex of the monocation $P(AuPR_3)_4{}^+$.

Lately, an unusual route to naked[7] phosphorus-containing ligands was presented by Mays et al., who reacted $[\{Cp(CO)_2Mo\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1b**)[8] with group 15 trichlorides ECl_3 (E = P, As, Sb) to form the novel mixed group 15 element-containing tetrahedrane complexes $[\{Cp(CO)_2Mo\}_2(\mu,\eta^2\text{-}PE)]$ by elimination of LiCl and HCl.[9] The chromium analogue $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1a**) had not been described in the literature until we found an efficient method for its synthesis by the reaction of $[\{Cp(CO)_2Cr\}_2(\mu,\eta^2\text{-}P_2)]$ with superhydride ($LiBEt_3H$).[10a] Herein we report on the remarkable differences in the reaction behaviour of the corresponding anions of **1a** and **1b** with the transition metal electrophile $[(Ph_3P)AuCl]$ and the formation of the first phosphido-containing mixed metal Au^{I} complex in an unusual multi-centre bonding situation.

Results and Discussion

Both neutral complexes **1a** and **1b** were converted into the corresponding anions under identical conditions using KH (Scheme 1). Subsequent reaction with $[(Ph_3P)AuCl]$ leads, in the case of the molybdenum complex **1b**, to substitution of a hydrogen atom by a $AuPPh_3$ moiety to form $[\{Cp(CO)_2Mo\}_2(\mu\text{-}H)\{\mu_3\text{-}P(H)Au(PPh_3)\}]$ (**2**). However, for the chromium homologue **1a** a rearrangement of the $[CpCr(CO)_2P]$ units is observed with formation of the novel trinuclear Au cluster **3** with a $Au_3Cr_6P_3$ core.

Complex **2** forms orange and **3** brown crystals, which are slightly soluble in hexane and readily soluble in toluene, CH_2Cl_2 and THF. In their IR spectra the CO stretching frequencies are observed in the typical range for terminal CO ligands. Additionally, a P−H stretching frequency is found for **2** at 2243 cm^{-1}. In the EI mass spectrum of **2** only characteristic fragment ion peaks could be detected, whereas for **3** no such fragments were found. Due to the quadrupolar moment of the ^{197}Au nucleus only two broad singlets at δ = 41.0 and 73.1 ppm are observed in the $^{31}P\{^1H\}$ NMR spectrum of **2** and one for **3** at δ = 38 ppm.

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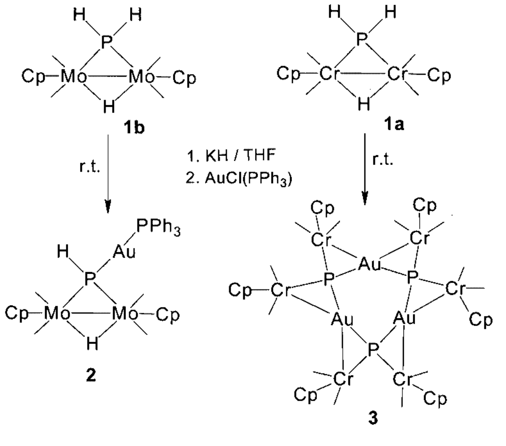

Scheme 1. Different reaction behaviour of dinuclear complexes $[\{Cp(CO)_2M\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ [M = Cr (**1a**), Mo (**1b**)] with $AuCl(PPh_3)$ (CO ligands are represented by bond lines)

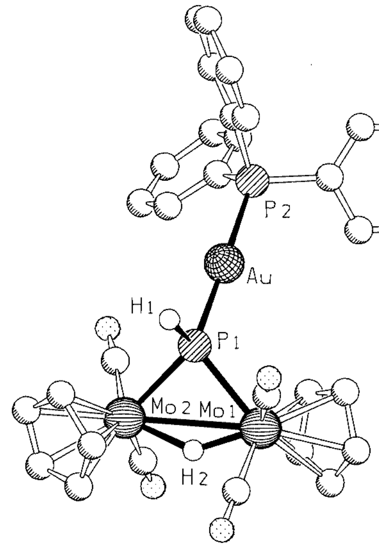

Figure 1. Molecular structure of **2**; hydrogen atoms of the Ph and Cp substituents are omitted for clarity; selected bond lengths [Å] and angles [°]: Mo(1)−Mo(2) 3.266(2), Mo(1)−P(1) 2.434(2), Mo(2)−P(1) 2.450(2), Au−P(1) 2.309(2), Au−P(2) 2.324(2); P(1)−Au−P(2) 179.15(7), Mo(1)−P(1)−Mo(2) 83.92(7), Mo(1)−P(1)−Au 119.24(9), Mo(2)−P(1)−Au 127.7(1)

The ^1H NMR spectrum of **2** shows a characteristic peak at high field ($\delta = -11.73$ ppm) for the bridging hydride ligand. This signal is split into a doublet due to the coupling with the phosphorus atom ($^2J_{H,P} = 29$ Hz). The PH proton also splits into a doublet which is detected at $\delta = 6.12$ ppm ($^1J_{H,P} = 282$ Hz). Two discrete singlets for the Cp protons at $\delta = 4.84$ and 5.04 ppm suggest a *trans* arrangement of the two Cp ligands as found in the solid-state structure of **2**.

The dinuclear $[Mo_2(CO)_4Cp_2]$ fragment of **2** (Figure 1) is bridged by a hydrido and a $PH(AuPPh_3)$ ligand. The Au atom is almost linearly surrounded by its substituents (P1−Au−P2 179.15(7)°). The Mo−Mo distance is 3.266(2) Å and is similar to that in the neutral complex **1b** [3.282(1) Å].[8b] The Mo−P bond lengths of 2.450(2) and 2.434(2) Å in **2** are only slightly longer than that in the starting material **1b** [2.402(1) Å]. The Au−P distances in **2** are almost identical [Au−P1 2.309(2) Å; Au−P2 2.324(2) Å]. Similar bond lengths are found in the structurally related compounds $[(CO)_8M_2(\mu\text{-}H)(\mu_3\text{-}PCy)Au(PPh_3)]$ [M = Mn, Re; Cy = cyclohexyl; M = Mn: Au−P1 2.306(1) Å and Au−P2 2.317(1) Å; M = Re: Au−P1 2.313(4) Å, Au−P2 2.303(4) Å].[11]

The X-ray structure analysis of **3** (Figure 2) reveals a planar Au_3P_3 six-membered ring (mean deviation of the atoms from the plane: 0.077 Å), where each of the distorted tetrahedrally surrounded phosphido ligands are bound to two Au atoms as well as to two $CpCr(CO)_2$ moieties. The Au atoms by themselves form an isosceles triangle with the closest distances between the atoms Au2 and Au3 of 3.284(1) Å; the other distances are 3.454(1) and 3.482(1) Å indicating essentially no Au···Au interaction.[6,12] The Au−P bond lengths of **3** are between 2.405(4) Å and 2.440(4) Å and are therefore longer than those found in the square pyramidal-coordinated P atoms of $P(AuPR_3)_5^{2+}$ [13] [2.295(3) Å for the axial P−Au bond and 2.356(3)−2.379(3) Å for the other] and $(R_3PAu)_4PAuP(AuPR_3)_4^{3+}$ [14] [2.293(7) Å (axial) and 2.369(3) Å for the other]. The Au−Cr distances of **3** [2.707(2)−2.748(3) Å] are in the range of those distances found in linear-coordinated Au−$CrCp(CO)_3$-containing complexes.[15] Significant structural features of **3** are the very short Cr−P bond lengths of 2.135(5)−2.168(4) Å, which are much shorter than the average Cr−P bond lengths in the related complexes $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)_2]$ (2.381 Å),[10b] $[(CO)_4CrP(CH_3)_2]_2$ (2.318 Å)[16] and in $[\{Cp(CO)_2Cr\}_2(\mu,\eta^2\text{-}P_2)]$ (2.409 Å),[17] $[\{Cp(CO)_2Cr\}_2(\mu,\eta^2\text{-}P_2)\{Cr(CO)_5\}]$ (2.405 Å)[18] and $[\{Cp(CO)_2Cr\}_2(\mu,\eta^2\text{-}P_2)\{Cr(CO)_5\}_2]$ (2.411 Å).[19] They are

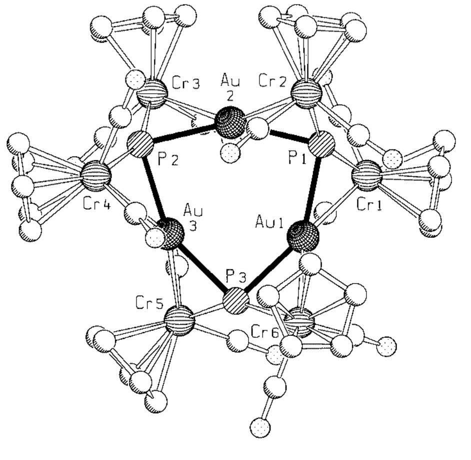

Figure 2. Molecular structure of **3**; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Au(1)−P(1) 2.413(3), Au(1)−P(3) 2.405(4), Au(2)−P(1) 2.399(4), Au(2)−P(2) 2.382(4), Au(3)−P(2) 2.408(4), Au(3)−P(3) 2.440(4), Au(1)−Cr(1) 2.725(3), Au(1)−Cr(6) 2.723(3), Au(2)−Cr(2) 2.730(3), Au(2)−Cr(3) 2.726(2), Au(3)−Cr(5) 2.707(2), Au(3)−Cr(4) 2.748(3), Cr(1)−P(1) 2.135(5), Cr(2)−P(1) 2.154(4), Cr(3)−P(2) 2.168(4), Cr(4)−P(2) 2.163(4), Cr(5)−P(3) 2.167(4), Cr(6)−P(3) 2.171(5); Au(1)−P(1)−Au(2) 91.75(12), Au(2)−P(2)−Au(3) 86.58(12), Au(1)−P(3)−Au(3) 91.96(12), P(1)−Au(1)−P(3) 143.92(13), P(2)−Au(2)−P(1) 153.13(12), P(2)−Au(3)−P(3) 151.00(12), Cr(1)−P(1)−Cr(2) 154.9(2), Cr(4)−P(2)−Cr(3) 154.2(2), Cr(5)−P(3)−Cr(6) 150.8(2)

even shorter than the Cr−P bond length in **1a** [2.266(1) and 2.271(1) Å],[10a] where the Cr−Cr bond is additionally clamped by the μ-H ligand.

Due to these remarkable structural features of **3**, including the unexpected existence of the Au−Cr bonding in this Au^I complex together with the fact that the phosphido atoms of **3** are substituted by only two 15 valence electron $Cp(CO)_2Cr$ units, we first speculated about the existence of additional H bridges between the Au and Cr atoms. Since we found no spectroscopic indication for this, we decided to perform density functional calculations[20] of a hypothetical complex $[\{Cp(CO)_2Cr\}_6(\mu\text{-}H)_6\{(\mu_4\text{-}P)_3Au_3\}]$ (**3a**) with a tentative X-ray structure and various other structures as starting points. This led to a large distribution of hydrogen positions showing Cr−H, Au−H, P−H and Cp−H bonds for different minimum structures of similar energies (some within 20 kJ/mol). The approximate C_3 symmetry of the $(AuP)_3$ ring was always heavily distorted and the bond lengths deviated considerably from the experimental values [d(Au−P) = 2.40−2.72 Å; d(Cr−P) = 2.14−2.39 Å; d(Au−Cr) = 2.75−2.98 Å]. We thus examined the structure of **3** by DFT calculations which resulted in close agreement with the experimental data [d(Au−P) = 2.49−2.56 Å; d(Cr−P) = 2.16−2.19 Å; d(Au−Cr) = 2.75−2.81 Å]. The computed bond lengths exceed the experimental values as is typical for the BP86 functional method, particularly for weak bonds involving Au atoms. The latter are stabilised by attractive dispersion forces, which are not accounted for in DFT.

The bond lengths in **3** and the Cr−P−Cr angle (151−155°) together with the electron count of Cr point to an unusual electronic structure, which is difficult to disentangle due to the low molecular symmetry. Mullikan occupancies[20f] for the valance orbitals 3p(P), 3d(Cr) and 6s(Au) are all close to one (0.8−1.2), which implies that they are all involved in bonding. The three-centre shared electron number[20g,20h] PCrAu = 0.16 indicates pronounced multicentre bonding. These facts may be rationalised by the following simplified picture: the 3p orbitals of (formal) P^{3-} are delocalised to form partial σ- and π-bonds to Cr with π-bonds delocalised into 6s(Au), leading to short P−Cr, relatively long Au−P and weak Au−Cr bonds.

Conclusions

The reported results confirm our observations in the reactivity studies of the tetrahedral P_2-containing complexes $[\{Cp(CO)_2M\}_2(\mu,\eta^2\text{-}P_2)]$ [M = Cr (**4a**), Mo (**4b**)] towards inorganic and organometallic complexes, where we found significant differences due to the lability of the Cr−Cr bond in **4a**[21] in comparison to the more stable Mo−Mo bond of **4b**.[22] Moreover, the molybdenum complex **1b** follows its general reactivity pattern towards transition metal electrophiles of the type $[L_nM'X]$ [X = Cl, Br; L_nM' = $Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO_2)Fe$, $(CO)_5Mn$] to give complexes of the type $[\{Cp(CO)_2M\}_2(\mu\text{-}H)(\mu_3\text{-}PH)M'L_n]$ in which transition metal phosphorus bonds are formed while retaining the Mo−Mo bond.[23] However, due to the high lability of the Cr−Cr bond in **1a** this complex appears to be a good synthon for the generation of flexible $[PCr(CO)_2Cp]$ units, and thus is a valuable starting material in cluster chemistry.

Experimental Section

General Remarks: All manipulations were performed under an atmosphere of dry N_2 using standard Schlenk techniques. The solvents were dried by common methods and freshly distilled prior to use. The starting materials $[\{Cp(CO)_2Mo\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$[24] $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$[10a] and $[(Ph_3P)AuCl]$[25] were prepared according to literature methods. NMR: Bruker AC 250 (^1H, 250.13 MHz; ^{31}P, 101.256 MHz); standard Me_4Si (^1H), 85% H_3PO_4 (^{31}P). MS: Finnigan MAT 311 ADF at 70 eV. IR: Bruker IFS 28 FT−IR spectrometer.

$[\{Cp(CO)_2Mo\}_2(\mu\text{-}H)(\mu_3\text{-}PH)Au(PPh_3)]$ (2): KH (0.04 g, 1.00 mmol) was added to a solution of $[\{Cp(CO)_2Mo\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1b**; 0.35 g, 0.75 mmol) in 25 mL of THF and the solution was stirred at room temperature for 30 minutes. During this time the solution turned deep purple due to the formation of the anion $[\{Cp(CO)_2Mo\}_2(\mu\text{-}PH_2)]^-$. After filtration, $[(Ph_3P)AuCl]$ (0.37 g, 0.75 mmol) was added to the filtrate and the reaction mixture was stirred for another 14 hours. The solvent was then removed completely in vacuo, and the residue was dissolved in a small quantity of CH_2Cl_2. Separation of the reaction mixture by TLC (hexane/CH_2Cl_2 2:1) in a glove box yielded an orange fraction containing a small amount of starting material **1b** and a red fraction of **2**. Recrystallisation from CH_2Cl_2 yielded **2** as orange crystals (0.21 g, 33%). ^1H NMR (300 MHz, [D$_6$]benzene, TMS): δ = −11.73 (d, $^2J_{H,P}$ = 29 Hz, 1 H, MoHMo), 4.84 (s, 5 H, Cp), 5.04 (s, 5 H, Cp), 6.12 (d, $^2J_{H,P}$ = 282 Hz, 1 H; PH), 7.93−7.47 (m, 15 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, [D$_6$]benzene, H_3PO_4): δ = 41.0 (s, br), 73.1 (s, br) ppm. MS (EI, 140 °C): *m*/*z* (%) = 467 (22) [M^+ − $AuPPh_3$], 443 (1) [M^+ − $AuPPh_3$ − CO], 406 (9) [$Mo_2(CO)_3Cp_2^+$], 378 (24) [$Mo_2(CO)_2Cp_2^+$], 350 (51) [$Mo_2(CO)Cp_2^+$], 322 (16) [$Mo_2Cp_2^+$], 262 (100) [PPh_3^+]. IR (KBr): ν(PH) = 2243 (w), ν(CO) = 1916 (vs), 1831 (vs) cm^{-1}.

$[\{Cp(CO)_2Cr\}_6\{(\mu_4\text{-}P)_3Au_3\}]$ (3): A solution of $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1a**; 0.46 g, 1.21 mmol) in 15 mL of THF was added to a solution of KH (0.12 g, 3.02 mmol) in 10 mL of THF and the mixture was stirred for 2 h at room temperature. The colour changed from dark green to bluish green due to the formation of the anion $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)]^-$. The unchanged KH was filtered off and the filtrate was stirred with $[(PPh_3)AuCl]$ (0.6 g, 1.21 mmol) for 3 h. The solvent was then removed in vacuo. Chromatographic separation on a silica gel column (35 × 2.5 cm) with *n*-hexane/toluene (2:1) gave a dark green fraction containing unchanged $[\{Cp(CO)_2Cr\}_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1a**) (0.15 g, 33%). Elution with *n*-hexane/CH_2Cl_2 (1:10) yielded a reddish brown fraction of $[\{Cp(CO)_2Cr\}_6\{(\mu_4\text{-}P)_3Au_3\}]$ (**3**) (0.13 g, 40%). IR (CH_2Cl_2): ν(CO) = 1930 (s), 1903 (vs) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]benzene, TMS): δ = 4.29 (s, 30 H, C_5H_5) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, [D$_6$]benzene, H_3PO_4): δ = 38 ($\omega_{1/2}$ = 1200 Hz) ppm. $C_{42}H_{30}Au_3Cr_6O_{12}P_3$ (1722.49): calcd. C 29.29, H 1.76; found C 28.98, H 1.83.

X-ray Crystallographic Study

2: $C_{32}H_{27}AuMo_2O_4P_2$, $M = 926.32$, crystal dimensions $0.20 \times 0.20 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$ (No. 2); $a = 8.8953(18)$, $b = 13.989(3)$, $c = 14.925(3)$ Å, $\alpha = 63.72(3)°$, $\beta = 83.99(3)°$, $\gamma = 72.64(3)°$, $T = 200(1)$ K, $Z = 2$, $V = 1588.6(6)$ Å^3, $D_c = 1.937$ Mg/m^3, μ(Mo-K_α) = 5.519 mm^{-1}, 9502 independent reflexes ($R_{\mathrm{int}} = 0.1125$, $2\theta_{\max} = 48°$), 378 parameters, $R_1 = 0.0573$ for 4310 observed reflections with $F_o = 4\sigma(F_0)$, $wR_2 = 0.1486$ for all reflections.

3: $C_{42}H_{30}Au_3Cr_6O_{12}P_3$, $M = 1722.47$, crystal dimensions $0.08 \times 0.04 \times 0.02$ mm^3, monoclinic, space group $P2_1$ (No. 4); $a = 12.268(3)$, $b = 15.996(3)$, $c = 13.010(3)$ Å, $\beta = 117.32(3)°$, $T = 193(1)$ K, $Z = 2$, $V = 2268.4(8)$ Å^3, $D_c = 2.522$ Mg/m^3, μ(Mo-K_α) = 11.206 mm^{-1}, 11802 independent reflexes ($R_{\mathrm{int}} = 0.0621$, $2\theta_{\max} = 51.94°$), 591 parameters, $R_1 = 0.0474$ for 7060 observed with $F_o = 4\sigma(F_0)$, $wR_2 = 0.1152$ for all reflections.

Crystal structure analyses of **2** and **3** were performed on a STOE IPDS diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with the program SHELXS-97,[26a] and full-matrix least-squares refinement on F^2 in SHELXL-97[26b] was performed with anisotropic displacements for non-H atoms, except for the C14 atom of **3**. Hydrogen atoms at the carbon atoms were located in idealised positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus and molybdenum atoms of **2** were refined freely. Although different crystals of **3** from different reactions were measured the same results were obtained to refine the data sets of **3** in the acentric space group $P2_1$ as inversion twins in an occupancy ratio of 53:47. All attempts to refine the structure in the centric space groups $P2_1/m$ or $P2_1/c$ failed.

CCDC-194528 (**2**) and CCDC-194529 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.uk/retrieving.htlm [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

DFT Calculations

All calculations were carried out using the BP86[20a] functional and the RI-J technique[20b] of the program package TURBOMOLE.[20c] C_1 symmetry and the SV(P)[20d] basis set were used throughout. Calculations with the TZVP[20e] basis set showed similar results.

Acknowledgments

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The authors thank the Degussa AG for the gift of precious metal compounds.

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Received January 30, 2003
[I03052]