

H⁺/AuPPh₃⁺ Exchange for the Hydride Complexes CpMoH(CO)₂(L) (L = PMe₃, PPh₃, CO). Formation and Structure of [Cp(CO)₂(PMe₃)Mo(AuPPh₃)₂]⁺[BF₄][−]

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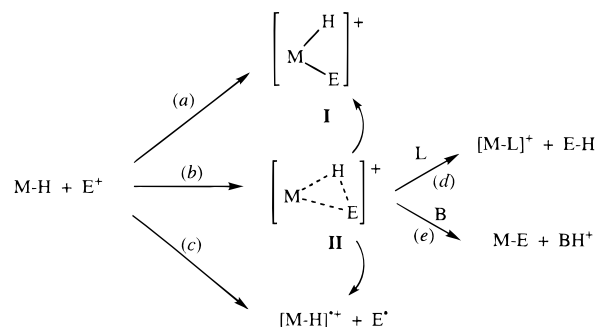
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The reaction of CpMoH(CO)₂L with AuPPh₃⁺BF₄[−] in THF at −40 °C proceeds directly to the MoAu₂ cluster compounds [CpMo(CO)₂L(AuPPh₃)₂]⁺BF₄[−] (L = PMe₃ (**1**), PPh₃ (**2**)) with release of protons. A 1:1 reaction leaves 50% of the starting hydride unreacted. At lower temperature, however, the formation of a [CpMo(CO)₂-(PMe₃)(μ-H)(AuPPh₃)]⁺ intermediate is observed. This compound evolves to the cation of **1** and CpMoH(CO)₂-(PMe₃) upon warming and is deprotonated by 2,6-lutidine to afford CpMo(CO)₂(PMe₃)(AuPPh₃). The X-ray structure of **1** can be described as a four-legged piano stool with the PMe₃ and the “η²-(AuPPh₃)₂” ligands occupying relative trans positions. [Cp(CO)₂(PMe₃)Mo(AuPPh₃)₂]⁺[BF₄][−] (*M_r* = 1298.41): monoclinic, space group *P*2₁/*n*, *a* = 18.1457(13) Å, *b* = 9.7811(7) Å, *c* = 26.096(2) Å, β = 105.086(5)°, *V* = 4472.0(5) Å³, *Z* = 4. The reaction of CpMoH(CO)₂(PMe₃) with 3 equiv of AuPPh₃⁺ affords a MoAu₃ cluster, [CpMo(CO)₂(PMe₃)-(AuPPh₃)₃]²⁺ (**3**), in good yields under kinetically controlled conditions. Under thermodynamically controlled conditions, **3** dissociates extensively into **1** and free AuPPh₃⁺. It is proposed that the hydride ligand helps build higher nuclearity Mo–Au clusters. The difference in reaction pathways for the interaction of AuPPh₃⁺ with CpMoH(CO)₂L when L = PR₃ or CO and for the interaction of CpMoH(CO)₂(PMe₃) with E⁺ when E = H, Ph₃C or AuPPh₃ is discussed. The lower acidity and greater aurophilicity of the [CpMo(CO)₂L(μ-H)(AuPPh₃)]⁺ intermediate when L = PMe₃ favor attack by AuPPh₃⁺ before deprotonation.

Introduction

Electrophilic addition is a well-known type of reaction in organometallic chemistry,^{1,2} and the addition of a variety of electrophiles to transition metal hydride complexes has been extensively investigated. A typical example of this reaction is protonation, which can occur either at the metal center or at a M–H bond, resulting in the formation of a classical (**I**, Scheme 1 path *a*) or nonclassical (**II**, path *b*) hydride complex, respectively.^{3,4} The formation of **I** may be preceded by the formation of **II**.⁵ The presence of other ligands (e.g. donor solvents) may lead to the substitution of H₂ from **II** (path *d*), and the overall reaction is therefore classified as an electrophilic abstraction. A second extensively investigated electrophilic reagent is the trityl cation. In this case, intermediate **II** is not observed, the reaction typically leading to electrophilic abstraction with formation of Ph₃CH.^{6–9} However, depending on the oxidation potential of the substrate, electron transfer may also occur (path *c*) leading to a 17-electron hydride intermediate and trityl radical, which then evolve according to a variety of

Scheme 1



reaction pathways.¹⁰ Finally, metal-based electrophiles (e.g. Cu⁺, Tl⁺, Ag⁺, AuL⁺) have received some attention, especially the gold-based cation AuPPh₃⁺. In this case, stable complexes of type **II** have been isolated and characterized in numerous occasions.^{11–24} Whenever these adducts are not stable, the

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typical pattern is deprotonation (path e) resulting in the overall replacement of an H^+ with the isolobal $AuPPh_3^+$ unit.

While each of the above mentioned electrophilic reagents have been investigated with a variety of transition metal hydride systems, there is apparently no single hydride complex for which all of the above reagents have been tested. Thus, it is not clear whether the different chemical reactivity should be attributed to differences in the nature of the electrophile or to differences in the hydride substrate. The class of compounds $CpMoH(CO)_2L$ ($L = PMe_3, PPh_3$) has been investigated by us and others in terms of oxidation (either chemical or electrochemical),^{8,25} protonation,²⁵ and hydride abstraction with the trityl cation.^{8,9,25} Reactions with metal-based electrophiles have not, however, been investigated. We report here our observations on the interaction with the gold-based electrophile $AuPPh_3^+$. Interesting differences have been observed with respect to the interaction of H^+ and Ph_3C^+ with the same substrates, as well as relative to the interaction of $AuPPh_3^+$ with $CpMoH(CO)_3$.

Experimental Section

General Methods. All operations were carried out under an atmosphere of dinitrogen or argon with standard Schlenk-line techniques. Solvents were purified by conventional methods and distilled under argon prior to use (THF and Et_2O from Na/benzophenone, heptane from Na, CH_2Cl_2 from P_4O_{10} , and MeCN from CaH_2). FT-IR spectra were recorded on a Perkin-Elmer 1880 spectrophotometer with CaF_2 or CsI cells. NMR spectra were obtained with Bruker WP200 and AF200 spectrometers. The peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (1H) or downfield of external 85% H_3PO_4 (^{31}P). For each ^{31}P NMR spectrum, a sealed capillary containing H_3PO_4 was immersed in the same NMR solvent used for the measurement, and this was used as reference. The elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ, and by Atlantic Microlab, Norcross, GA. Compounds Ph_3PAuCl ,²⁶ $CpMoH(CO)_2(PMe_3)$,²⁷ $CpMoH(CO)_2(PPh_3)$,²⁸ and $CpMo(CO)_3(AuPPh_3)$ ²⁹ were prepared as previously published. $AgBF_4$ was purchased from Aldrich and used without further purification. All NMR data for the new compounds are collected in Table 1.

Preparation of $[CpMo(CO)_2(PMe_3)(AuPPh_3)_2]BF_4$, 1. To a solution of $(PPh_3)AuCl$ (178 mg; 0.378 mmol) in 3 mL of THF was added a solution of $AgBF_4$ (70.1 mg; 0.378 mmol) in 5 mL of THF. The $AgCl$ precipitate was filtered off through Celite. The colorless solution was cooled to $-40^\circ C$ and solid $CpMoH(CO)_2(PMe_3)$ (53 mg; 0.18 mol) was added, resulting in an immediate change to bright yellow. After 1 h, the solution was filtered, concentrated by evaporation under reduced pressure to a final volume of ca. 3 mL, and stored at $-20^\circ C$. A yellow microcrystalline precipitate was obtained (97 mg, 42% yield). Anal. Calc for $C_{46}H_{44}Au_2BF_4MoO_2P_3$: C 42.55; H 3.42. Found: C 42.37, H 3.54. IR (CH_3CN , cm^{-1}): 1855 s, 1792 s. IR (THF, cm^{-1}): 1851 s, 1788 s. IR (Nujol mull, cm^{-1}): 1850 br, 1757 br. Recrys-

Table 1. NMR Data for All New Compounds

compd ^a	1H NMR in CD_3CN	1H NMR in acetone- d_6	$^{31}P\{^1H\}$ NMR in CD_3CN	$^{31}P\{^1H\}$ NMR in acetone- d_6
$[CpMo(CO)_2(PMe_3)(AuPPh_3)_2]^+ (1)$	7.5–7.3 (m, 30H, Ph), 5.46 (d, 5H, $J_{PH} = 1.4$ Hz, Cp), 1.64 (d, 9H, $J_{PH} = 10.1$ Hz, Me)	7.7–7.4 (m, 30H, Ph), 5.71 (s, 5H, Cp), 1.78 (d, 9H, $J_{PH} = 10$ Hz, Me) ^b	49.5 (d, 2P, $J_{PP} = 10.2$ Hz, PPh_3), 20.9 (t, 1P, $J_{PP} = 10.2$ Hz, PMe_3)	49.7 (d, 2P, $J_{PP} = 11.0$ Hz, PPh_3), 24.6 (t, 1P, $J_{PP} = 11.0$ Hz, PMe_3) ^b
$[CpMo(CO)_2(PPh_3)(AuPPh_3)_2]^+ (2)$	7.5–7.2 (m, 45H, Ph), 5.27 (s, 5H, Cp) ^c	7.7–7.3 (m, 45H, Ph), 5.42 (s, 5H, Cp)	62.1 (t, 1P, $J_{PP} = 8.7$ Hz, $MoPPh_3$), 47.6 (d, 2P, $J_{PP} = 8.7$ Hz, $AuPPh_3$) ^c	66.4 (t, 1P, $J_{PP} = 8.7$ Hz, $MoPPh_3$), 47.6 (d, 2P, $J_{PP} = 8.7$ Hz, $AuPPh_3$)
$[CpMo(CO)_2(PMe_3)(AuPPh_3)_3]^{2+} (3)$	7.6–7.2 (m, 45H, Ph), 5.96 (d, 5H, $J_{PH} = 1.4$ Hz, Cp), 1.64 (d, 9H, $J_{PH} = 10.5$ Hz, Me)	7.7–7.2 (m, 45H, Ph), 6.51 (s, 5H, Cp), 1.78 (d, 9H, $J_{PH} = 10$ Hz, Me) ^d	51.9 (br, 2P, PPh_3) 51.1 (br, 1P, PPh_3), 20.6 (br, 1P, PMe_3)	54.7 (br, 2P, PPh_3), 53.7 (br, 1P, PPh_3), 27.4 (t, 1P, $J_{PP} = 9.0$ Hz, PMe_3) ^d
$[CpMo(\mu-H-AuPPh_3)(CO)_2(PMe_3)]^+ (4)$	7.5 (br, 15H, Ph), 5.39 (s, 5H, Cp), 1.62 (d, 9H, $J_{PH} = 10$ Hz, Me), –5.63 (br, d, $J_{PH} = 24$ Hz, MoH)		50.1 (br, PPh_3), 19.3 (br, PMe_3)	
$CpMo(AuPPh_3)(CO)_2(PMe_3) (5)$	7.5–7.4 (m, 15H, Ph), 5.39 (s, 5H, Cp), 1.60 (d, 9H, $J_{PH} = 9.6$ Hz, Me)		47.7 (br, PPh_3), 21.5 (br, PMe_3)	
$[CpMo(CO)_3(AuPPh_3)]^+ (6)$		7.7–7.4 (m, 30H, Ph), 5.87 (s, 5H, Cp)		50.5 (s)
$[CpMo(CO)_3(AuPPh_3)_2]^+ (7)$		7.7–7.4 (m, 45H, Ph), 5.98 (s, 5H, Cp)		53.7 (s, 2P), 53.2 (s, 1P)

^a The counterion is BF_4^- for each cationic compound. ^b $T = 218$ K. ^c $T = 245$ K. ^d $T = 190$ K.

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tallization from CH₂Cl₂/heptane yielded yellow needles of **1** suitable for X-ray analysis.

Preparation of [CpMo(CO)₂(PPh₃)(AuPPh₃)₂]BF₄, **2.** The synthesis was carried out by a procedure identical to that described above for **1**, starting from CpMoH(CO)₂(PPh₃) (155 mg, 0.304 mmol) and 2 equiv of a AuPPh₃⁺ solution in THF, to yield compound **2** in 58% yield. Anal. Calc for C₆₁H₅₀Au₂BF₄MoO₂P₃: C 49.35, H 3.39. Found: C, 49.15; H, 3.80. IR (THF, cm⁻¹): 1868 s, 1807 s. The CD₃CN solution shows evidence for decomposition (formation of a dark precipitate) after recording the NMR spectrum.

Reaction of CpMoH(CO)₂(PMe₃) with 3 equiv of [AuPPh₃]BF₄. Preparation of [CpMo(CO)₂(PMe₃)(AuPPh₃)₃](BF₄)₂, **3.** A colorless solution of [AuPPh₃]BF₄ obtained from (PPh₃)AuCl (207 mg, 0.418 mmol) and AgBF₄ (81.4 mg, 0.418 mmol) in 15 mL of THF was filtered through Celite, cooled to -40 °C, and added dropwise to an equally cooled solution of CpMoH(CO)₂(PMe₃) (41 mg, 0.14 mmol) in 2 mL of THF. All subsequent operations until isolation of the final product were carried out at -40 °C. A lemon yellow solid formed initially but redissolved upon further stirring for 1 h. After filtration, the solution was evaporated under reduced pressure to a final volume of ca. 2 mL. Addition of heptane (25 mL) yielded the product as a pale yellow precipitate. The suspension was chilled to -80 °C for 2 h and filtered. The solid was washed with heptane (2 × 5 mL) and dried *in vacuo*. Yield: 219 mg, 89%. The room-temperature ³¹P-NMR in CD₃CN showed the expected resonances. However, they were broader relative to the low-temperature spectrum in acetone-*d*₆, and decomposition occurred upon prolonged data acquisition. The isolated solid was not stable at room temperature under N₂ for extensive periods of time, changing color to a paler yellow and losing crystallinity. A satisfactory elemental analysis could not be obtained.

Interaction between **1 and AuPPh₃⁺.** A solution of [AuPPh₃]BF₄ was prepared *in situ* as described above from (PPh₃)AuCl (5 mg, 0.01 mmol) and AgBF₄ (2 mg, 0.01 mmol) in THF (3 mL). After filtration, the colorless solution was chilled to -40 °C and compound **1** (13 mg, 0.01 mmol) was added. Compound **1** dissolved immediately to yield a lemon-yellow solution. After being stirred at -40 °C for 1/2 h, the solution was evaporated to dryness under reduced pressure. The residue was investigated by ¹H-NMR in CD₃CN, revealing a mixture of **1** and **3** in a 1.25:1 ratio. The ³¹P-NMR spectrum also revealed the presence of **1** and **3** and of unreacted AuPPh₃⁺.

Reaction of CpMoH(CO)₂(PMe₃) with 1 equiv of AuPPh₃⁺ in THF at Low Temperature and Subsequent Treatment with 2,6-Lutidine. Formation of [CpMo(CO)₂(PMe₃)(μ-H)(AuPPh₃)₂]BF₄, **4, and CpMo(CO)₂(PMe₃)(AuPPh₃), **5**.** A solution of [AuPPh₃]BF₄ was prepared *in situ* as described above from (PPh₃)AuCl (42 mg, 0.085 mmol) and AgBF₄ (16.5 mg, 0.085 mmol) in THF (6 mL). After filtration, the colorless solution was cooled to -60 °C and CpMoH(CO)₂(PMe₃) (25 mg, 0.085 mmol) was added. A clear yellow solution formed immediately. After being stirred at -60 °C for 1/2 h, the solution was evaporated to dryness under reduced pressure and the oily residue was washed with precooled (-60 °C) heptane (5 mL). This treatment resulted in the crystallization of the residue, which was then investigated by ¹H-NMR after dissolution in precooled CD₃CN (0.5 mL). After dissolution, the solution was transferred into a thin-walled 5 mm NMR tube which was frozen in a dry ice/acetone bath and thawed to room temperature only prior to introduction into the NMR probe. The ¹H-NMR showed the presence of compound **4** as the major product; minor resonances for compound **1** are also present. Following the recording of this spectrum, an excess amount (ca. 30 μL) of 2,6-lutidine was added to the NMR tube and the ¹H-NMR spectrum was recorded again, showing disappearance of the chemical shifts of **4** and appearance of new chemical shifts due to compounds **5**, CpMoH(CO)₂(PMe₃) [¹H-NMR: 5.21 (s, Cp), 1.48 (d, PMe₃, J_{PH} = 10 Hz), and -6.24 (d, Mo-H, J_{PH} = 60.5 Hz). ³¹P-NMR: 21.9 (s); these values correspond to those reported in the literature],²⁷ and AuPPh₃(2,6-lutidine)⁺ [³¹P-NMR: 29.6]. From the ³¹P-NMR, the approximate relative ratio of these compounds is 10:1:5. Mixing fresh solutions of AuPPh₃⁺ and 2,6-lutidine in CD₃CN gave a resonance at δ 31.1.

Reaction of CpMoH(CO)₂(PMe₃) with AuPPh₃⁺ and 2,6-Lutidine in a 1:1:1 Ratio. Formation of Compound **5.** A solution of [AuPPh₃]-BF₄ was prepared *in situ* as described above from (PPh₃)AuCl (53.8 mg, 0.108 mmol) and AgBF₄ (21.2 mg, 0.108 mmol) in THF (3 mL).

The mixture was filtered through Celite, and the filter cake was washed with an additional 3 mL of THF. In another Schlenk tube was prepared a solution of CpMoH(CO)₂(PMe₃) (32 mg, 0.108 mmol) and 2,6-lutidine (12.6 μL, 0.108 mmol) in THF (2 mL). The AuPPh₃⁺ solution was transferred to the solution of the Mo hydride and lutidine, resulting in a color change to canary-yellow. After being stirred at room temperature for 1/2 h, the solution was evaporated to dryness under reduced pressure to leave an oily residue which was washed with heptane (4 × 5 mL) and dried. This material was investigated by ¹H- and ³¹P-NMR in CD₃CN. The major resonances in the ¹H- and ³¹P-NMR spectra are due to compound **5**. Strong resonances of the starting compound CpMoH(CO)₂(PMe₃) are also visible (in a ca. 2:3 ratio relative to the MoAu compound), as well as two resonances of the 2,6-lutidinium ion at δ 8.14 (t, 1H, *p*-H, J_{HH} = 7.9 Hz) and 2.69 (s, 6H, Me). The 2,6-lutidinium resonance for the *m*-H protons, which should be observed at δ 7.59 (d, J_{HH} = 8 Hz; from a genuine sample), is masked by the stronger phenyl resonances. The isolation of the CpMo(CO)₂(PMe₃)-(AuPPh₃) compound in a pure crystalline state could not be achieved.

Reaction of CpMo(CO)₃(AuPPh₃) with [AuPPh₃]BF₄. Formation of Complexes [CpMo(CO)₃(AuPPh₃)₂]BF₄ (6**) and [CpMo(CO)₃(AuPPh₃)₃](BF₄)₂ (**7**).** A solution of [AuPPh₃]BF₄ was prepared *in situ* as described above from (PPh₃)AuCl (28 mg, 0.057 mmol) and AgBF₄ (11 mg, 0.057 mmol) in THF (7 mL). After filtration through Celite, the colorless solution was added dropwise to a solution of CpMo(CO)₃(AuPPh₃) (40 mg, 0.057 mmol) in 1 mL of THF. The solution changed color from orange-red to a paler orange while a gray solid dropped out of solution. After being stirred at room temperature for 1 h and filtration, the solution was evaporated to dryness under reduced pressure and the residue was investigated by NMR in acetone-*d*₆. The ¹H-NMR shows the phenyl signals in the δ 7.67–7.42 range and four Cp resonances at δ 5.98, 5.87, 5.57, and 5.42 (starting compound). The ³¹P-NMR shows resonances at δ 55.5 (starting compound), a resonance at δ 50.5 (assigned to complex **6**), two additional resonances in a 2:1 ratio at δ 53.7 and 53.2 (assigned to complex **7**), and a resonance at δ 39.2 (AuPPh₃⁺). These assignments are justified in the Results section.

X-ray Analysis of Compound **1.** A canary yellow crystal with dimensions 0.50 × 0.20 × 0.075 mm was placed and optically centered on the Enraf-Nonius CAD-4 diffractometer. The crystal final cell parameters and orientation matrix were determined from 25 reflections in the range 17.6 < θ < 19.3° and confirmed with axial photographs. Data were collected with ω scans over the range 2.46 < θ < 24.96° in the ±*h*, -*k*, *l* octants, resulting in the measurement of 9060 reflections, of which 7835 unique [*R*(int) = 0.0674]. The data were corrected for Lorenz and polarization factors and for absorption on the basis of eight ψ-scan reflections (transmission factors range 0.1433–0.2790).³⁰ A decay correction was not necessary. All crystallographic calculations were performed on a personal computer with the SHELXTL package of programs. The space group was uniquely determined as *P*2₁/*n* by the systematic absences. Direct methods located the heavy atoms (Mo, 2 Au, 3 P) and the BF₄ group. The structure was refined and completed by alternating full-matrix least-squares cycles and difference-Fourier maps. Hydrogen atoms were placed in calculated positions and used for structure factor calculations but not refined; these positions were constantly updated. All of the non-hydrogen atoms were refined anisotropically, and the structure was refined to convergence (Δ/*σ* ≤ 0.002). A final difference-Fourier map possessed many peaks as large as |Δρ| ≤ 2.50 e Å⁻³ near the heavy atoms, namely the Mo and Au atoms. The remainder of the map was essentially featureless with |Δρ| ≤ 0.86 e Å⁻³ indicating that the structure is both correct and complete. The function minimized during the refinement was Σw(*F*_o² - *F*_c²), where *w* = 1/[σ²(*F*_o²) + (0.0857*P*)² + 9.43*P*] and *P* = (max(*F*_o², 0) + 2*F*_c²)/3. An empirical correction for extinction was also applied to the data in the form (*F*_c², corr) = *k*[1 + 0.001*xF*_c²λ³/sin(2θ)]^{-1/4} where *k* = 0.082 72 is the overall scale factor. The value determined for *x* was 0.00043(9). The relevant crystal and refinement parameters are collected in Table 2, and selected bond distances and angles are listed in Table 3.

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Table 2. Crystal Data for Compound **1**

formula	C ₄₆ H ₄₄ Au ₂ BF ₄ MoO ₂ P ₃
fw	1298.41
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	18.1457(13)
<i>b</i> , Å	9.7811(7)
<i>c</i> , Å	26.096(2)
β, deg	105.086(5)
<i>V</i> , Å ³	4472.0(5)
<i>Z</i>	4
<i>d</i> _{calc} , Mg/m ³	1.928
μ(Mo Kα), mm ⁻¹	6.982
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
temp, °C	153(2)
transmissn factors: max, min	0.2790, 0.1433
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0520, <i>wR</i> 2 = 0.1293
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.0650, <i>wR</i> 2 = 0.1364

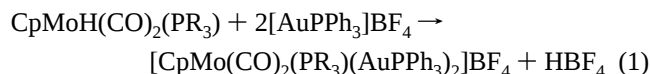
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

Au(1)–Au(2)	2.7384(5)	Mo(1)–C(6)	1.989(9)
Au(1)–Mo(1)	2.7859(8)	Mo(1)–C(7)	1.985(10)
Au(1)–P(1)	2.284(2)	C(6)–O(6)	1.151(11)
Au(2)–Mo(1)	2.7791(8)	C(7)–O(7)	1.162(12)
Au(2)–P(2)	2.296(2)	Au(1)···C(6)	2.414(9)
Mo(1)–P(3)	2.457(3)	Au(2)···C(7)	2.430(9)
Mo(1)–CNT	2.018(10)		
Au(2)–Au(1)–Mo(1)	60.40(2)	Au(2)–Mo(1)–C(6)	96.1(3)
Au(2)–Au(1)–P(1)	131.36(6)	Au(2)–Mo(1)–C(7)	58.5(3)
Mo(1)–Au(1)–P(1)	167.74(6)	Au(2)–Mo(1)–CNT	110.6(3)
Au(1)–Au(2)–Mo(1)	60.65(2)	P(3)–Mo(1)–C(6)	75.7(3)
Au(1)–Au(2)–P(2)	124.46(6)	P(3)–Mo(1)–C(7)	75.1(3)
Mo(1)–Au(2)–P(2)	174.85(6)	P(3)–Mo(1)–CNT	109.6(3)
Au(1)–Mo(1)–Au(2)	58.95(2)	C(6)–Mo(1)–C(7)	101.3(4)
Au(1)–Mo(1)–P(3)	133.52(7)	C(6)–Mo(1)–CNT	133.6(4)
Au(1)–Mo(1)–C(6)	57.9(3)	C(7)–Mo(1)–CNT	124.9(4)
Au(1)–Mo(1)–C(7)	109.7(3)	Mo(1)–C(6)–O(6)	169.8(8)
Au(1)–Mo(1)–CNT	104.4(3)	Mo(1)–C(7)–O(7)	168.0(8)
Au(2)–Mo(1)–P(3)	130.55(7)		

Results

(a) Synthesis and NMR Characterization. The reaction of CpMoH(CO)₂(PR₃) with [AuPPh₃]₂BF₄ in a 1:2 ratio in THF solution at –40 °C yields compounds [CpMo(CO)₂(PR₃)(AuPPh₃)₂]₂BF₄ (*R* = Me (**1**), Ph (**2**)), see eq 1. The isolated

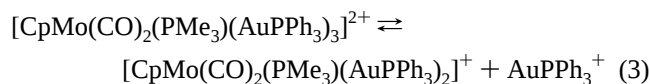
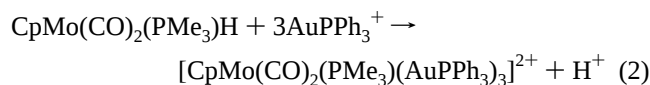


yields are only 42% (*R* = Me) and 58% (*R* = Ph), but an NMR investigation indicates that substantial amounts of the products are still present in solution and that no byproducts are formed in the reactions. When the reactions are carried out with a 1:1 Mo/Au ratio, the same products are formed and 50% of the Mo starting materials remain unreacted as shown by NMR. The THF-solvated protons that form during the reaction are not sufficiently acidic to protonate the residual hydride compound. It has previously been shown²⁵ that compounds CpMoH(CO)₂-(PR₃) (*R* = Me, Ph) are less basic than water and that their protonation in dry, low-basicity solvents results in the evolution of H₂. No gas evolution, on the other hand, was observed for reaction 1. IR and NMR monitoring of the reactions indicates the replacement of the starting material with the final product without the buildup of new resonances that could be attributed to intermediates.

The products are soluble in most organic solvents and the solutions are stable for brief periods of time. Slow decomposition, however, takes place, even at –80 °C, to yield unidentified materials. The nature of the products as MoAu₂ clusters is

indicated by the stoichiometry of the reaction, by the analytical data, and by NMR spectroscopy. In particular, two ³¹P-NMR resonances in a 2:1 doublet:triplet ratio are observed and attributed to the two AuPPh₃ and the Mo(PR₃) units, respectively. Coupling between the two types of phosphorus nuclei is weak, as expected from the three bond separation, but easily observable (*J*_{PP} is ca. 11 Hz for **1** and 9 Hz for **2**). The IR spectra exhibit two absorptions that are red shifted by ca. 60–80 cm⁻¹ relative to those of the corresponding starting material. This shows that the two Au(PPh₃)⁺ moieties are withdrawing less electron density relative to a single H⁺ or, taking a different point of view, that the [AuPPh₃]₂ unit donates more electron density than the H⁻ ligand. In addition, the structure of compound **1** has been confirmed by a single-crystal X-ray investigation (*vide infra*).

The PMe₃ system allowed the synthesis of a trigold derivative, [CpMo(CO)₂(PMe₃)(AuPPh₃)₃](BF₄)₂, **3**. This product formed selectively in high yields by reacting complex CpMoH(CO)₂-(PMe₃) with 3 equiv of AuPPh₃⁺ at low temperatures; see eq 2. Under the same conditions, the interaction of **1** with an



additional 1 equiv of AuPPh₃⁺ also results in the formation of **3**, but only an apparent equilibrium between **3** and unreacted **1** and AuPPh₃⁺ is reached (1/3 ca. 1.25:1). Compound **3** is not stable either in solution or in the solid state. For this reason, a satisfactory elemental analysis could not be obtained on this compound. Nevertheless, the NMR investigation of the freshly isolated material confirms its purity. Upon standing in solution, slow formation of **1** and AuPPh₃⁺ is observed by NMR, confirming the existence of equilibrium 3. Other decomposition products, however, are also formed, including the known³¹ [Au₈(PPh₃)₉]³⁺ (³¹P-NMR: δ 51 in CD₃CN). This was obtained as a precipitate from crystallization attempts of compound **3** and was identified by comparison with the ³¹P-NMR chemical shift reported in the literature³² and by its characteristic green color.

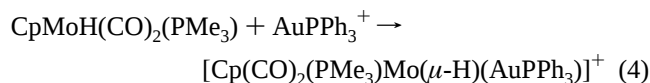
The main characteristic of the NMR spectrum of **3** is the inequivalence of the AuPPh₃ units (two resonances in a 2:1 ratio are observed). This indicates *C_s* symmetry (either static or dynamic) for the molecule and excludes a dynamic *C_{3v}* symmetry. Both types of symmetry are documented for MAu₃ clusters.¹⁴ The PMe₃ signal shows coupling to only two PPh₃ units, but the two PPh₃ resonances are broad and their coupling pattern is not clearly discernible. This is not unusual, the same phenomenon being observed in other cases, for instance [Au₅-ReH₄(PPh₃)₇]²⁺.¹²

In view of the various mechanistic possibilities for the formation of **1** and **2** which will be examined in the Discussion section, additional experiments were carried out. When the reaction between CpMoH(CO)₂(PMe₃) and AuPPh₃⁺ was carried out in a 1:1 ratio in THF at –70 °C, the formation of an intermediate hydride-containing species was observed. Attempts to isolate this compound were unsuccessful, as the complex decomposes upon warming the THF solution. The formation

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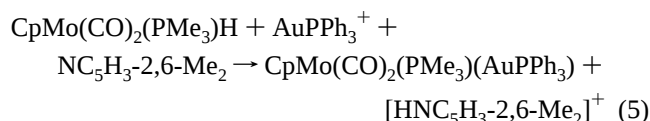
(32) Bruce, D. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1990**, 29, 1313–1319.

of compound **1** as a minor product was also observed. The downfield shift of the hydride signal (δ −5.63) and the reduced J_{PH} of 24 Hz with respect to the starting compound point to the formulation of this derivative as [Cp(CO)₂(PMe₃)Mo(μ -H)(AuPPh₃)]BF₄, **4**; see eq 4. The hydride resonance is coupled

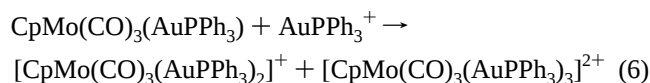


to only one P nucleus. We suspect that this coupling is due to the P nucleus of the PMe₃ ligand. The lack of coupling with the P nucleus of AuPPh₃ could be due to fast chemical exchange with free AuPPh₃⁺. The ³¹P-NMR spectrum shows the PMe₃ resonance at δ 19.3 [cf. 24.5 for CpMoH(CO)₂(PMe₃)] and the PPh₃ resonance at 50.1, the latter overlapping with the PPh₃ resonance of compound **1**.

When the reaction between CpMo(CO)₂(PMe₃)H and AuPPh₃⁺ in THF was carried out in a 1:1 ratio at room temperature in the presence of the stoichiometric amount of 2,6-lutidine, a single new compound was formed instead of the 1:1 mixture of **1** and unreacted hydride complex (*vide supra*). This product is characterized by two ³¹P-NMR resonances in a 1:1 ratio at δ 47.7 and 21.5 and does not show any hydride resonance in the ¹H-NMR, indicating the formation of CpMo(CO)₂(PMe₃)(AuPPh₃), **5**; see eq 5. The *in situ* generation of **4** followed by the addition of lutidine also leads to the formation of **5**.



The interaction between compound **1** and HBF₄·Et₂O in MeCN at room temperature or in acetone-*d*₆ at −60 °C leads to partial decomposition and formation of large amounts of compound **3**. Finally, the previously reported²⁹ CpMo(CO)₃(AuPPh₃) compound was treated with 1 equiv of AuPPh₃⁺. A combination of ¹H- and ³¹P-NMR monitorings indicated the formation of both compounds [CpMo(CO)₃(AuPPh₃)₂][BF₄], **6**, and [CpMo(CO)₃(AuPPh₃)₃](BF₄)₂, **7**, while some [AuPPh₃]⁺ remained unreacted (eq 6). Compound **6** is characterized by a



single ³¹P-NMR resonance at δ 50.5 (cf. 49.5 for **1** and 47.6 for **2**), while compound **7** is characterized by two resonances in a 2:1 ratio at δ 53.7 and 53.2 (cf. 54.7 and 53.7 for compound **3**). By comparison, the ³¹P-NMR resonance of free [AuPPh₃]⁺ is at δ 39.2, and that of the starting complex CpMo(CO)₃(AuPPh₃) is at δ 55.5 in the same solvent (acetone-*d*₆).

(b) X-ray Characterization. The chemical nature of compound **1** is verified by an X-ray crystallographic study, which also establishes the stereochemistry around the Mo center. A side view of the cation is shown in Figure 1, and selected bond distances and angles are in Table 3. The ion contains a MoAu₂ triangle, with Mo–Au distances averaging 2.76(2) Å and an Au–Au distance of 2.7384(5) Å. The Mo–Au distances are longer than that reported for (η^5 -C₅H₄CHO)Mo(CO)₃(AuPPh₃) [i.e. 2.7121(5) Å],³³ as expected from the electron deficiency of the MoAu₂ unit in **1**. The Au–Au distance is typical of clusters containing a 3c–2e MAu₂ unit, values in the range

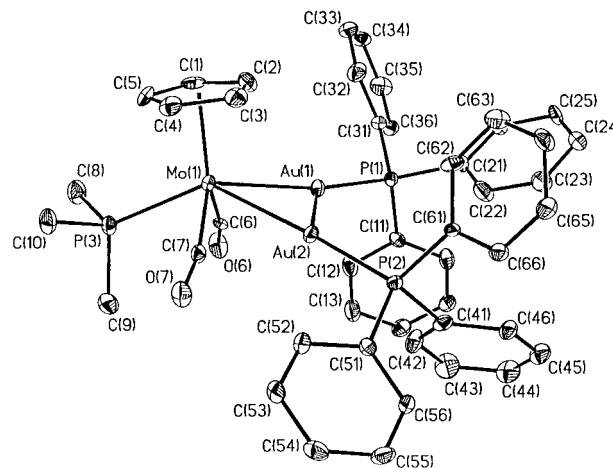


Figure 1. Top view of the [CpMo(CO)₂(PMe₃)(AuPPh₃)₂]⁺ cation of compound **1** with the numbering scheme employed. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 40% probability level.

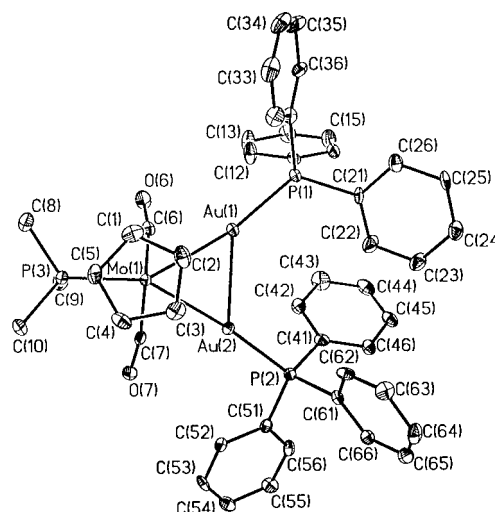


Figure 2. Side view of the cation of compound **1**. Drawing parameters are as in Figure 1.

2.728–3.028 Å having been found previously.²⁴ Each Au atom is further bonded to one terminal PPh₃ ligand, while the Mo atom is further bonded to a Cp ring, two CO ligands, and a PMe₃ ligand. An alternative way to view the structure, which can better be appreciated from the top view in Figure 2, is to consider the (AuPPh₃)₂ grouping as a ligand for the Mo(II) center in a *trans* four-legged piano stool geometry which would then be related to an hypothetical (η^2 -H₂) complex. The “ η^2 -(AuPPh₃)₂” ligand adopts a parallel stereochemistry relative to the plane of the Cp ring. When viewed in this light, the distortions of the four “legs” follow the typical pattern,³⁴ with the two CO ligands being bent away from the Cp ligand to a greater extent [average CNT–Mo–CO angle = 129(5)°] than the PMe₃ and “ η^2 -(AuPPh₃)₂” ligands [the bending of the “ η^2 -(AuPPh₃)₂” ligand is measured at the center point X of the Au–Au bond as CNT–Mo–X = 110.1(3)°].

Discussion

The reaction of AuPPh₃⁺ with compounds CpMoH(CO)₂L (L = PMe₃ or PPh₃) follows a very different path relative to the reactions of the isolobal electrophilic reagents H⁺ and Ph₃C⁺. While the H⁺ and Ph₃C⁺ electrophiles lead to the formal

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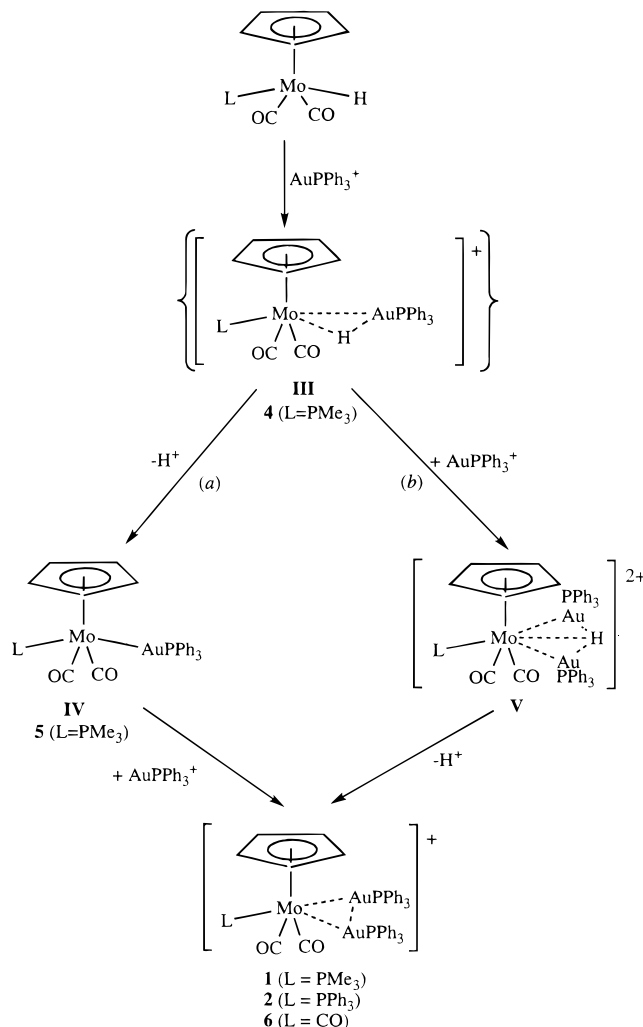
abstraction of the hydride ligand as H^- , the interaction with AuPPh_3^+ leads to the ultimate departure of the hydride ligand as H^+ as previously established for other transition metal hydride complexes.²³ Specific examples are the formation of $\text{CpM}(\text{CO})_3(\text{AuPPh}_3)$ from $\text{CpMH}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),²⁹ $[\text{Pt}(\text{AuPPh}_3)_2\text{Cl}(\text{PEt}_3)_2]^+$ from *trans*- $\text{PtHCl}(\text{PEt}_3)_2$,³⁵ and $\text{Os}_4(\mu\text{-H})_2(\mu\text{-AuPR}_3)_2(\text{CO})_{12}$ from $\text{Os}_4(\mu\text{-H})_3(\mu\text{-AuPR}_3)(\text{CO})_{12}$.³⁶ In addition, the reaction continues with further addition of the AuPPh_3^+ electrophilic fragments, building up digold- and even trigold-molybdenum clusters. This behavior may be attributed to the well-known aurophilicity of gold.³⁷

The identification of compound **4** from the low-temperature reaction (eq 4) is a clear indication that the first step of the reaction leading to **1** and **2** is the addition of the electrophilic AuPPh_3^+ to the Mo-H bond. This also corresponds to the accepted path of attack of other electrophilic reagents such as H^+ and Ph_3C^+ on the M-H bond, and in addition, many analogous complexes containing a $3\text{c-}2\text{e}$ MHAu moiety are sufficiently stable and have been isolated (see Introduction and Scheme 1). However, compound **4** then undergoes exchange of a proton with the isolobal AuPPh_3^+ unit. This exchange could in principle take place either via a dissociative mechanism (i.e. deprotonation to form intermediate **IV** before addition of the second AuPPh_3^+ , see path *a* in Scheme 2) or via an associative intermediate such as **V** (path *b* in Scheme 2). Intermediate **III** corresponds to the cation of compound **4** when $\text{L} = \text{PMe}_3$.

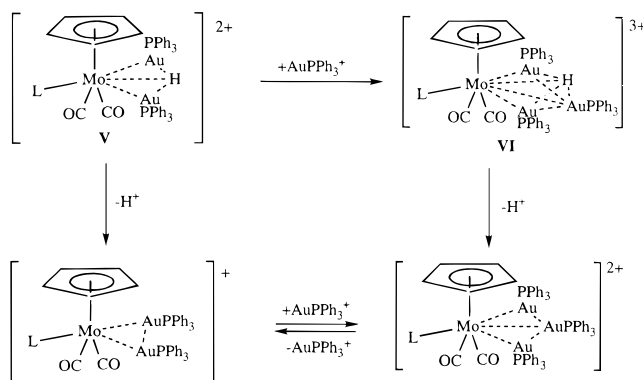
It is interesting to observe that **IV** is the stable observed product of the reaction when $\text{L} = \text{CO}$,²⁹ whereas it is not observed as an intermediate when $\text{L} = \text{PMe}_3$. However, such system is indeed obtained (compound **5**) when the reaction is carried out in the presence of a strong base (eq 5). Since the acidity of **III** should decrease in the order $\text{L} = \text{CO} < \text{PMe}_3$, while the aurophilicity of **III** should correspondingly increase, it seems most likely that the formation of **1** and **2** proceeds according to path *b* of Scheme 2. A third possible pathway would involve disproportionation of **III** to afford the product, starting complex, and H^+ . This corresponds to the electrophilic attack of **III** by another **III** and is therefore quite unlikely relative to the proposed attack by AuPPh_3^+ , because the latter reagent is a stronger electrophile and is present at a higher concentration.

The formation of the trigold cluster **3** deserves greater attention. The interaction between **1** and AuPPh_3^+ in a 1:1 ratio forms the desired **3**, but a substantial amount of starting materials remain unreacted, indicating the presence of an equilibrium (eq 3). The direct interaction of $\text{CpMoH}(\text{CO})_2(\text{PMe}_3)$ and 3 equiv of AuPPh_3^+ , on the other hand, produces **3** in high yields without the formation of significant amounts of **1**. Once isolated, compound **3** is rather unstable and dissociates AuPPh_3^+ to generate **1**. These observations demonstrate that the formation of **3** via the direct interaction of $\text{CpMoH}(\text{CO})_2(\text{PMe}_3)$ and 3 equiv of AuPPh_3^+ proceeds via a pathway that does not involve the formation of **1**. One possible rationalization that appears attractive to us involves the interaction of the third AuPPh_3^+ unit with an intermediate such as **V** (see Scheme 3). The hydrogen atom could kinetically facilitate the incorporation of the third AuPPh_3^+ group via an intermediate such as **VI**. No detailed knowledge of stereochemistry for **V**, **VI**, and the final trigold product is implied in the drawings of Scheme 3. $3\text{c-}2\text{e}$ interactions are known to be established faster when H atoms

Scheme 2



Scheme 3



are present. For instance, the reductive elimination of R-H from an alkyl-hydride complex is faster than that of R-R from the corresponding dialkyl complex and the same is true for the reverse oxidative addition process, these reactions involving the formation of intermediates containing $3\text{c-}2\text{e}$ $[\text{MRX}]$ ($\text{X} = \text{H}$ or R) moieties.³⁸⁻⁴¹ This rate differences are believed to be

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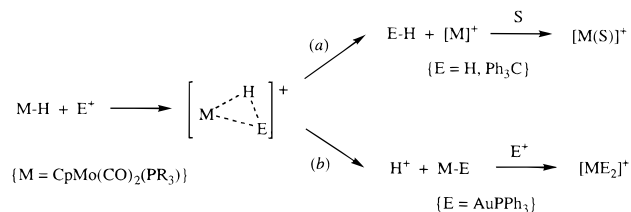
related to a greater ease of H migration because of the spherical symmetry of the 1s orbital used by H for bonding, whereas alkyl groups must require rehybridization in the transition state.^{42,43} Similar considerations, therefore, may be applied when comparing H with AuPPh₃. Other examples of additions of AuPPh₃⁺ to cationic hydride complexes, in many cases followed by deprotonation, have been reported.²³ To the best of our knowledge, however, the system described here is the first one leading, under kinetically controlled conditions, to a product which is unstable toward elimination of AuPPh₃⁺.

It is also interesting to observe the systematic increase in stability upon replacement of a H atom with a AuPPh₃ unit along the series of compounds [Cp(CO)₂LMoXY]⁺, where X and Y are either H or AuPPh₃ and the “MoXY” moiety establishes a 3c–2e bonding interaction. It was previously shown that the [CpMo(CO)₂(L)(η²-H₂)]⁺ complexes (L = PMe₃ or PPh₃), i.e. the presumed first products of the interaction between CpMoH(CO)₂L and H⁺, are not stable even at −80°C in noncoordinating solvents (e.g. toluene or heptane), the BF₄[−] counterion being sufficiently basic to displace the H₂ ligand from the coordination sphere.²⁵ On the other hand, complexes **1** and **2** are stable at room temperature in the crystalline state, whereas compound **4** has an intermediate stability. There are many other examples where a L_nM–H compound is less stable than the isolobal L_nM–AuPPh₃ analogue.²⁴ Following the description of the system with X = Y = H as a “dihydrogen” complex, compounds **1**, **2**, and **4** could also be formally described as σ-complexes of the hypothetical Ph₃PAu–AuPPh₃ and H–AuPPh₃ ligands, respectively.

Conclusion

For the first time, a comparison of the reactivity of the series of electrophilic reagents H⁺, Ph₃C⁺, and AuPPh₃⁺ with

Scheme 4



the same hydride substrates, i.e. CpMoH(CO)₂L (L = PMe₃, PPh₃, or CO), is available. The observed pathways parallel those previously reported for each reagent with other hydride substrates. While the first step is presumably the same in all cases with formation of a three-center–two-electron [MHE]⁺ moiety (E = electrophile), the harder electrophiles H⁺ and Ph₃C⁺ prefer to remain bonded to the harder base H[−] (path *a* in Scheme 4),^{8,25} whereas the softer electrophile AuPPh₃⁺ prefers to remain bonded to the softer base [M][−] (path *b* in Scheme 4). The nature of the observed final product in this case is dictated by the auriphilicity of the system. This study has also provided an example of the ligand effect on the acidity of the 3c–2e [MHAu] moiety: Spontaneous deprotonation occurs for [Cp(CO)₂LMo(μ-H)AuPPh₃]⁺ when L = CO, whereas the complex with L = PMe₃ can only be deprotonated by strong bases (e.g. 2,6-lutidine). Finally, evidence has been presented for the kinetic role of a hydrogen atom in building transition metal–gold clusters.

Acknowledgment. Support for this work by the Department of Energy (Grant No. DEFG059ER14230 to R.P.) is gratefully acknowledged. R.G. thanks the Italian Ministry of Education for a student fellowship and the University of Camerino for a leave.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for compound **1** is available on the Internet only. Access information is given on any current masthead page.

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