# Reactivity of Ruthenium and Niobium Trihydrides with Gold Fragments. Crystal Structure of the Hexanuclear Raft Cluster $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$†

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The reactions of $[MH_3(L)L'][M = Ru, L = \eta\text{-}C_5Me_5, L' = P(C_6H_{11})_3$ **1**; M = Nb, L = L' = $\eta\text{-}C_5H_4SiMe_3$ **2**; M = Nb, L = L' = $\eta\text{-}C_5H_3(SiMe_3)_2$-1,3 **3**] with $[Au(PPh_3)]PF_6$ produce the trinuclear clusters $[L(L')M(\mu\text{-}H)_2\{Au(PPh_3)\}_2]PF_6$ [L = $\eta\text{-}C_5Me_5$, L' = $P(C_6H_{11})_3$, M = Ru **4**; L = L' = $\eta\text{-}C_5H_4SiMe_3$, M = Nb **5**; L = L' = $\eta\text{-}C_5H_3(SiMe_3)_2$, M = Nb **6**]. Complex **1** also reacts with one or two equivalents of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ to yield respectively the neutral derivatives $[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)_2\text{-}Au(PPh_3)]$ **7** and $[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)\{Au(PPh_3)\}_2]$ **8**. The same reaction with $[NbH_3(\eta\text{-}C_5H_4SiMe_3)_2]$ yields the novel hexanuclear raft cluster $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9**. Spectroscopic (IR and NMR) data are provided for all the compounds. Crystals of **9** are triclinic, space group $P\bar{1}$, with $a = 14.927(2)$, $b = 15.083(2)$, $c = 15.632(2)$ Å, $\alpha = 103.81(1)$, $\beta = 99.20(1)$, $\gamma = 112.55(1)°$, and $Z = 2$. The molecule consists of a central almost equilateral triangle of gold atoms, with each Au–Au bond bridged by a niobium atom which completes its co-ordination sphere with two $\eta\text{-}C_5H_4SiMe_3$ groups. Additionally, each Au–Nb is bridged by one hydride ligand. The most interesting feature of this molecule is the planarity of the six metal atoms.

We have recently reported[1] the preparation of a series of trihydride complexes of niobium and ruthenium. These compounds were shown to exhibit anomalous NMR properties characterized by the observation of $AB_2$ spectra for the hydrides involving large (up to 160 Hz) temperature-dependent AB coupling constants. These properties have been encountered by others in ruthenium and iridium chemistry[2] and have been rationalized recently as being the result of exchange coupling between protons. In a search for a chemical characterization of the phenomenon, we have explored the chemistry of these derivatives in detail. A first approach was to attempt to discriminate hydrides from co-ordinated dihydrogen in potential hydrido dihydrogen complexes using Lewis acids such as $[(CuCl)_n]$ or $[Cu(MeCN)_4]BF_4$.[3] Another concerns the selective substitution of a proton in the co-ordination sphere of ruthenium or niobium by a '$AuL^+$' fragment.[4] This approach could also lead to novel bimetallic dihydrogen derivatives. Mixed-metal clusters containing both gold and a late transition metal have been known for several years and Pignolet and co-workers[5] have recently developed the chemistry of ruthenium–gold derivatives. These compounds were shown to exhibit interesting hydrogen-transfer reactions and this prompted us to study the preparation of new species of this type.

In this paper we describe the synthesis and structural characterization of a series of new bimetallic hydride clusters associating gold and ruthenium or niobium. A preliminary account of the X-ray crystal and electronic structure of the raft cluster $[Au_3Nb_3(\mu\text{-}H)_6(\mu\text{-}C_5H_4SiMe_3)_6]$ **9** has been reported.[6]

## Results and Discussion

*Reactions of Trihydride Derivatives with Cationic Gold Complexes.*—Complexes $[MH_3(L)L']$ **1–3** [equation (1)] were treated with $[Au(PPh_3)]PF_6$, prepared *in situ* in tetrahydrofuran (thf) from $Au(PPh_3)Cl$ and $TlPF_6$, as a model reaction for protonation. Previously the protonation of $[RuH_3\{P(C_6H_{11})_3\}(\eta\text{-}C_5Me_5)]$ **1** had been shown to lead to an unstable dihydrogen compound from which further dehydrogenation occurred.[7] However, whatever the stoichiometry {molar ratio $[Au(PPh_3)]^+$: complex, 1:1 or 2:1} or reaction conditions employed only the 2:1 adduct $[L(L')M(\mu\text{-}H)_2\text{-}\{Au(PPh_3)\}_2]PF_6$ was obtained. The trinuclear clusters were

$$[MH_3(L)L'] + 2[Au(PPh_3)]PF_6 \longrightarrow [L(L')M(\mu\text{-}H)_2\{Au(PPh_3)\}_2]PF_6 + HPF_6 \quad (1)$$

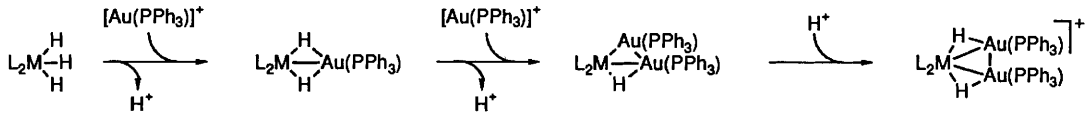
| | M | L | L' | |
|---|---|---|---|---|
| **1** | Ru | $\eta\text{-}C_5Me_5$ | $P(C_6H_{11})_3$ | **4** |
| **2** | Nb | $\eta\text{-}C_5H_4SiMe_3$ | $\eta\text{-}C_5H_4SiMe_3$ | **5** |
| **3** | Nb | $\eta\text{-}C_5H_3(SiMe_3)_2$ | $\eta\text{-}C_5H_3(SiMe_3)_2$ | **6** |

isolated in high yields as stable yellow-orange crystals after recrystallization. The different steps involved in the formation of these compounds are proposed in Scheme 1.

The first and second steps suppose substitution processes,

† Hexa-μ-hydrido-1:2$\kappa^2H$; 2:3$\kappa^2H$; 3:4$\kappa^2H$; 4:5$\kappa^2H$; 5:6$\kappa^2H$; 1: 6$\kappa^2H$-hexakis[1,1,3,3,5,5($\eta^5$)-(trimethylsilyl)cyclopentadienyl]trigold(I)triniobium(III) (3 *Au–Au*) (6 *Au–Nb*).

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1

**Table 1** Proton NMR spectra in the hydride region and $^{31}P$ NMR spectra

| | $^1H^a$ | | | $^{31}P^b$ |
|---|---|---|---|---|
| Complex | δ | System | $J$(P–H)/Hz | δ(ppm) |
| **4**[c] | −8.60 (2 H) | AA′XX′Y | 47 ($J_{P^xH}$)[d] | 77.96(t) $P(C_6H_{11})_3$ |
| | | | 18 ($J_{P^yH}$) | 45.5(d) $PPh_3$ |
| **5**[c] | −3.81 (2 H) | AA′XX′ | 39 ($J_{P^1H}$) | |
| | | | 7.5 ($J_{P^2H}$) | |
| **6**[c] | −3.85 (2 H) | AA′XX′ | 42 ($J_{P^1H}$) | |
| | | | 7 ($J_{P^2H}$) | |
| **7**[e] | −9.20 (2 H) | dd | 41 ($J_{P^1H}$) | 80.7(s) $P(C_6H_{11})_3$ |
| | | | 25 ($J_{P^2H}$) | 47.6(s) $PPh_3$ |
| **8**[e] | −10 (1 H) | ddd | 28 ($J_{P^AH}$)[f] | 79 $P^A(C_6H_{11})_3$[f] |
| | | | 33 ($J_{P^BH}$) | 42 $P^BPh_3$ |
| | | | 4 ($J_{P^CH}$) | 37.5 $P^CPh_3$ |
| **9**[e] | −2.90 (6 H) | s | | |

[a] Internal standard $SiMe_4$; values given in parentheses are intensities; s = singlet, d = doublet, t = triplet. [b] External standard $H_3PO_4$. [c] In $[^2H_6]$acetone. [d] See Fig. 1. [e] In $[^2H_6]$benzene. [f] See Fig. 4.

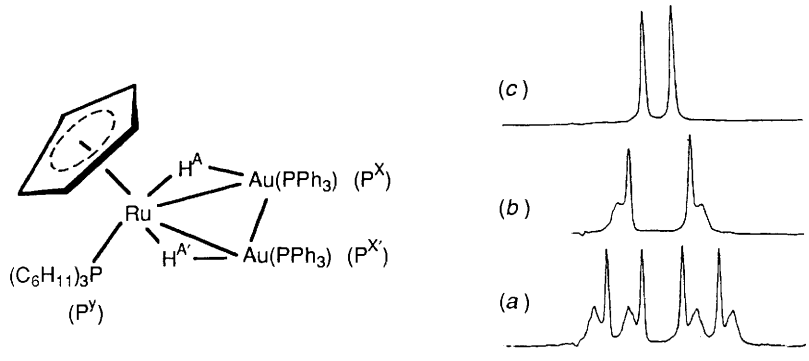



**Fig. 1** $^1H$ NMR spectrum of complex **4** in the hydride region. (*a*) Coupled with the phosphorus atoms (AA′XX′Y system), (*b*) decoupled from $P(C_6H_{11})_3(P^y)$; (*c*) decoupled from $PPh_3(P^x,P^{x'})$

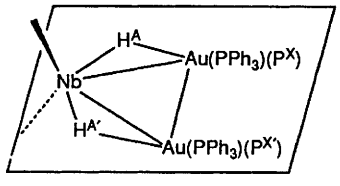



**Fig. 2**

and the third step protonation to give the final cationic trinuclear clusters **4**, **5** and **6**. All attempts to isolate and characterize the proposed neutral species were unsuccessful, probably because the protonation occurs readily in the acidic medium produced ($HPF_6$).

In conclusion, we were not able to mimic the protonation reaction by adding only one equivalent of $[Au(PPh_3)]^+$. Instead of the expected formation of $H_2$ we observed the substitution of $H^+$ by $[Au(PPh_3)]^+$. It is remarkable that both complexes **1** and **2** behave similarly towards $[Au(PPh_3)]^+$ as early and late transition metals seldom react in the same manner with a specific fragment.

This type of cluster has many precedents in transition-metal gold chemistry. For example Pignolet and co-workers[8] have recently reported the preparation of the dication $[(dppm)_2Ru(\mu\text{-}H)_2Au_2(PPh_3)]^{2+}$ [dppm = bis(diphenylphosphine)methane] whereas some of us have already reported[9] a preliminary account of the X-ray crystal structure of complex **5**.

The IR spectra of **5** and **6** show the characteristic absorptions for cyclopentadienyl[10] and trimethylsilyl[11] groups as well as other internal vibrations of the different groups. The IR spectrum of **4** shows the bridging hydrides as a broad band centred at 1710 $cm^{-1}$, the corresponding bands not being observed for **5** and **6**. Multinuclear NMR spectroscopy (Table 1) proved to be more efficient however for characterizing these complexes. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4** the $P(C_6H_{11})_3$ and $PPh_3$ groups appear as a triplet at δ 77.96 ($J_{PP}$ = 3.1 Hz) and a doublet at δ 45.5 respectively as expected for an $AX_2$ type spectrum. The two hydrides are equivalent and the $^1H$ NMR spectrum shows a doublet of doublets at δ −8.6 as expected for an AA′XX′Y type spectrum (see Fig. 1). Selective decoupling experiments of the phosphines allowed the determination of the different coupling constants. The two hydrides in complexes **5** and **6** are also equivalent and show AA′XX′ type $^1H$ NMR spectra (a doublet of complex signals) with peaks at δ −3.81 and −3.85 respectively in accord with the structure shown in Fig. 2.

The $^{13}C$ NMR spectrum of **5** shows a pattern (three resonances) observed previously for the various carbon atoms of the cyclopentadienyl ring for bis(trimethylsilylcyclopentadienyl)niobium derivatives[12] in which the ligands

located on the reflection plane have a symmetrical environment as in Fig. 2. Some of us have previously established[9] the molecular structure of **5** by an X-ray diffraction study although the hydride ligands were not located in the final structure. Proton NMR spectroscopy (at 80 MHz) also failed to locate the bridging hydride ligands.[9]

*Reactions of Trihydride Derivatives with Neutral Gold Complexes.*—In order to avoid the final protonation process we used the gold amide complex $[Au\{N(SiMe_3)_2\}(PPh_3)]$ as an alternative gold reagent.[13] An approach to the preparation of neutral mixed transition-metal gold clusters by reaction of the appropriate alkoxide or amide derivative with a polyhydride has been largely employed by Caulton and co-workers.[14]

Addition of one equivalent of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ to **1** leads to the formation of a yellow solution from which yellow microcrystals of $[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)_2Au(PPh_3)]$ **7** are obtained upon appropriate work-up (Scheme 2). Under the same experimental conditions but in the presence of two equivalents of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ we succeeded in isolating the neutral digold derivative $[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)\{Au(PPh_3)\}_2]$ **8** as orange crystals in high yield (Scheme 2). It is noteworthy that protonation of an isolated sample of **8** with one equivalent of $HPF_6$ leads to complex **4** as expected. This behaviour provides strong evidence for the third step proposed in Scheme 1. However, in the presence of three or more equivalents of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ complex mixtures (the main component of which was **8**) were obtained and we were unable to isolate an '$RuAu_3$' cluster cleanly.

The neutral ruthenium–gold mixed clusters **7** and **8** were isolated as air-sensitive crystalline materials. In their IR spectra they show bridging hydride stretches at 1730 and 1620 $cm^{-1}$ respectively.

The $^1H$ NMR spectrum of **7** shows the hydrides as a doublet of doublets at $\delta$ −9.2 $\{J_{HP}[P(C_6H_{11})_3]$ 25; $J_{HP}(PPh_3)$ 40.9 Hz$\}$. The magnitude of the $HAuPPh_3$ coupling constant indicates the presence of bridging $Ru(\mu\text{-}H)Au$ hydrides.[5] The signal due to $\eta\text{-}C_5Me_5$ is observed at $\delta$ 2.40 and the protons of the two phosphines at $\delta$ 7–8 ($PPh_3$) and 1.2–2.2 $[P(C_6H_{11})_3]$ (Fig. 3).

Dihydrido-bridged bimetallic gold-transition metal derivatives such as **7** are well documented, *e.g. cis*-$[AuRu(\mu\text{-}H)_2(dppm)_2(PPh_3)]^{+}$[15] but all such derivatives characterised previously were cationic and so it will be of interest to study the reactivity of the neutral species.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **8** shows three distinct phosphine resonances at $\delta$ 79 ($P_A$, d, $J_{AC}$ 17), 42 ($P_B$, d, $J_{BC}$ 21) and 37.5 ($P_C$, dd) attributed respectively to $P\{C_6H_{11})_3$, $PPh_3$ on the gold atom linked to the hydride and the $PPh_3$ on the bridging gold atom (see Fig. 4). The $^1H$ NMR spectrum of **8** shows a usually high-field resonance for the $\eta\text{-}C_5Me_5$ group at $\delta$ 2.65, phosphine signals at $\delta$ 7–8 ($PPh_3$) and 1.2–2.2 $[P(C_6H_{11})_3]$ and a hydride at $\delta$ −10 as a doublet of doublets of doublets. The coupling constants were attributed after selective decoupling experiments ($J_{HP_A}$ 28, $J_{HP_B}$ 33 and $J_{HP_C}$ 4 Hz). The absence of coupling between the phosphine located on the central gold and that on ruthenium is in agreement with the observation that the central hydride in complexes of type **1** is not coupled to phosphorus.[1a,b] This indicates that the geometrical disposition of the hydrides is responsible for this absence of coupling rather than any other factors.

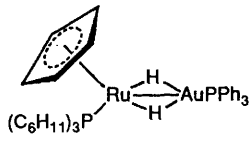
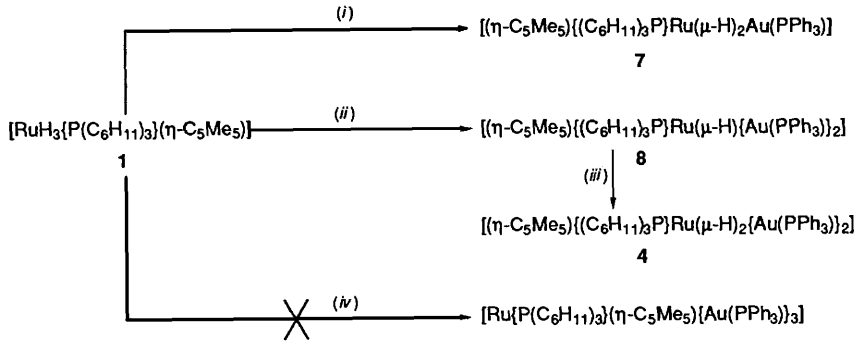



**Fig. 3**




**Scheme 2** (*i*) $[Au\{N(SiMe_3)_2\}(PPh_3)]$ 1 equiv., $-NH(SiMe_3)_2$; (*ii*) $[Au\{N(SiMe_3)_2\}(PPh_3)]$ 2 equiv., $-2NH(SiMe_3)_2$; (*iii*) $HPF_6$, (*iv*) $[Au\{N(SiMe_3)_2\}(PPh_3)]$ 3 equiv.

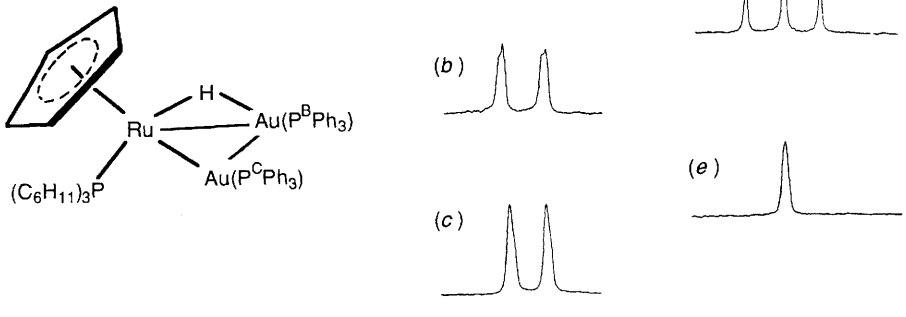



**Fig. 4** $^1H$ NMR spectrum of complex **8** in the hydride region. (*a*) Coupled with the phosphorus atoms (HABC system); (*b*) decoupled from $P(C_6H_{11})_3$ ($P^A$); (*c*) decoupled from $P^B$; (*d*) decoupled from $P^C$; (*e*) decoupled from $P^A$, $P^B$ and $P^C$

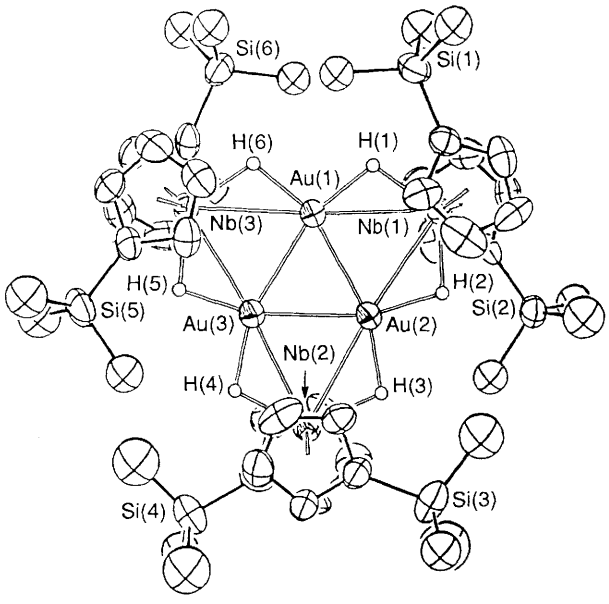



**Fig. 5** ORTEP view of the hexanuclear raft cluster $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$

In conclusion, complexes **7** and **8** represent a new class of neutral bimetallic derivative.

The niobium complex **2** exhibits a different behaviour towards the gold amide $[Au\{N(SiMe_3)_2\}(PPh_3)]$ than the ruthenium complex **1**. It reacts with one equivalent of this reagent [equation (2)] at room temperature to give a purple solution instantaneously from which very air-sensitive purple needles of the raft cluster $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9** were isolated [equation (2)].

$$[NbH_3(\eta\text{-}C_5H_4SiMe_3)_2] \xrightarrow{[Au\{N(SiMe_3)_2\}(PPh_3)]} \underset{\mathbf{2}}{} [(\eta\text{-}C_5H_4SiMe_3)_2Nb(\mu\text{-}H)_2Au(PPh_3)] \xrightarrow{-PPh_3} \tfrac{1}{3}[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6] \quad (2)$$
$$\mathbf{9}$$

Reaction of **2** with one equivalent of the gold amide must initially take place with the substitution of $H^+$ by $[Au(PPh_3)]^+$ to give a neutral compound analogous to that isolated in the case of ruthenium (*i.e.* **7**). However in the case of niobium this complex is probably unstable towards phosphine dissociation and rearrangement. We have undertaken an $^1H$ NMR study of this reaction and observed that initially the spectrum shows a resonance in the hydride region (doublet at δ −5.20, $J_{HP}$ = 25 Hz) which probably corresponds to the intermediate neutral cluster proposed in equation (2). The compound then transforms in solution and the resonance of the bridging hydrides of **9** is observed at δ −2.90. All attempts to stabilize this intermediate compound (at low temperature) were unsuccessful. A study (MO calculations) of the electronic *structure* of **9** indicates a striking electronic stabilization of its geometry. The most interesting feature of this compound is associated with the overlap of the $a_1'$ combination of the $(\eta\text{-}C_5H_4SiMe_3)_2Nb^+$ lone pair orbitals with the $2a_1'$ lowest-unoccupied molecular orbital (LUMO) of the gold–hydrogen unit that leads to an important contribution to Au–Au bonding which we believe accounts for the short Au–Au distance[6] and the overall stability of the compound.

In the IR spectrum of **9** no terminal M–H stretch is observable but in the $^1H$ NMR spectrum a hydride resonance appears as a singlet at δ −2.90 at all temperatures studied. A measure of relaxation time as a function of temperature gives a $T_1$ minimum of *ca.* 100 ms at 228 K.[16] This value is fairly low but similar values have been found in polynuclear polyhydride derivatives.[17] The $^1H$ NMR spectrum also shows an $SiMe_3$ resonance at δ 0.54 and the cyclopentadienyl protons as an AA′BB′ pattern at δ 4.99 and 5.48 ($J_{AB}$ 2.2 Hz).

The stability of the raft cluster **9** and our inability to isolate an analogous complex of ruthenium from complex **1** probably reflects a differing behaviour of the early- and late-transition metal towards the gold amide. However other factors, for example the presence of the bulky $P(C_6H_{11})_3$ in **1** cannot be excluded.

**Table 2** Selected bond lengths (Å) and angles (°) for $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9**

| | | | |
|---|---|---|---|
| Au(1)–Au(2) | 2.764(2) | Au(1)–Au(3) | 2.757(2) |
| Au(2)–Au(3) | 2.780(3) | Au(1)–Nb(3) | 3.033(3) |
| Au(1)–Nb(1) | 3.032(3) | Au(2)–Nb(2) | 2.989(2) |
| Au(2)–Nb(1) | 2.985(2) | Au(3)–Nb(3) | 2.967(2) |
| Au(3)–Nb(2) | 2.987(2) | Nb(1)–C(2) | 2.065(16) |
| Nb(1)–Cp(1) | 2.073(20) | Nb(2)–Cp(4) | 2.062(20) |
| Nb(2)–Cp(3) | 2.036(17) | Nb(3)–Cp(6) | 2.052(18) |
| Nb(3)–Cp(5) | 2.061(19) | Si(2)–C(9) | 1.843(17) |
| Si(1)–C(1) | 1.833(16) | Si(4)–C(25) | 1.838(18) |
| Si(3)–C(17) | 1.862(20) | Si(6)–C(41) | 1.850(13) |
| Si(5)–C(33) | 1.845(13) | | |
| Au(2)–Au(1)–Au(3) | 60.5(1) | Nb(1)–Au(1)–Nb(3) | 176.2(1) |
| Au(1)–Au(2)–Au(3) | 59.7(1) | Nb(1)–Au(2)–Nb(2) | 174.3(1) |
| Au(1)–Au(3)–Au(2) | 59.9(1) | Nb(2)–Au(3)–Nb(3) | 173.7(1) |
| Au(2)–Au(1)–Nb(1) | 61.8(1) | Au(2)–Au(1)–Nb(3) | 121.9(1) |
| Au(3)–Au(1)–Nb(3) | 61.4(1) | Au(3)–Au(1)–Nb(1) | 122.2(1) |
| Au(1)–Au(2)–Nb(1) | 63.5(1) | Au(1)–Au(2)–Nb(2) | 121.9(1) |
| Au(3)–Au(2)–Nb(2) | 62.2(1) | Au(3)–Au(2)–Nb(1) | 123.1(1) |
| Au(1)–Au(3)–Nb(3) | 63.9(1) | Au(1)–Au(3)–Nb(2) | 122.2(1) |
| Au(2)–Au(3)–Nb(2) | 62.3(1) | Au(2)–Au(3)–Nb(3) | 123.7(1) |
| Au(1)–Nb(1)–Au(2) | 54.7(1) | Au(2)–Nb(1)–Cp(1) | 109.5(5) |
| Au(1)–Nb(1)–Cp(1) | 106.6(5) | Au(2)–Nb(1)–Cp(2) | 105.5(5) |
| Au(1)–Nb(1)–Cp(2) | 108.9(5) | Cp(1)–Nb(1)–Cp(2) | 140.2(7) |
| Au(2)–Nb(2)–Au(3) | 55.4(1) | Au(3)–Nb(2)–Cp(3) | 106.4(5) |
| Au(2)–Nb(2)–Cp(3) | 105.5(5) | Au(3)–Nb(2)–Cp(4) | 105.6(5) |
| Au(2)–Nb(2)–Cp(4) | 107.4(5) | Cp′(3)–Nb(2)–Cp(4) | 143.2(8) |
| Au(1)–Nb(3)–Au(3) | 54.7(1) | Au(3)–Nb(3)–Cp(5) | 106.0(5) |
| Au(1)–Nb(3)–Cp(5) | 110.6(5) | Au(3)–Nb(3)–Cp(6) | 109.8(5) |
| Au(1)–Nb(3)–Cp(6) | 105.7(5) | Cp′(5)–Nb(3)–Cp(6) | 139.3(8) |

* Cp refers to the centre of the $C_5$ ring of $\eta\text{-}C_5H_4SiMe_3$.

*Crystal Structure of* $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9**.—An ORTEP view of complex **9** is shown in Fig. 5. The structure consists of an almost equilateral triangle of gold surrounded by a similarly equilateral niobium triangle. The Au–Au distance is very short (near 2.77 Å), shorter than that found for other clusters containing gold.[5] The placement of the hydrogen atoms in the positions shown is indicated by the residual electron density in the last Fourier-difference map. Location of the hydrogen atoms in these sites is chemically reasonable and has received strong theoretical support.[6]

The niobium–gold distance is larger than that found for the other known niobium–gold clusters [2.9139(8) and 2.9098(8) Å][9] and also larger than for other transition metal–gold clusters.[5] This reflects the relatively electron-poor character of the niobium centre. There are some precedents for raft structures of this type,[18] even for polyhydride clusters associating both transition-metal and coinage elements (Group 11).[18c–f] Recent papers by Calderazzo *et al.*[19] describe the preparation of niobium(0) or tantalum(0) fragments similarly located on the metal–metal bonds of a silver triangle.

## Conclusion

We were not able to detect the formation of an $\eta^2\text{-}H_2$ complex by use of $[Au(PPh_3)]^+$ as a proton analogue; instead, cationic $[MAu_2]^+$ (M = Nb or Ru) complexes **4**, **5** and **6** were obtained. Employing $[Au(PPh_3)]^+$ instead of $[Au\{N(SiMe_3)_2\}(PPh_3)]$

**Table 3** Final atomic coordinates ( $\times 10^4$) for the non-hydrogen atoms for $[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9**

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| Au(1) | 6 259(1) | 1 082(1) | 2 943(1) | C(19) | 2 846(14) | −2 952(13) | 315(11) |
| Au(2) | 4 187(1) | 398(1) | 2 436(1) | C(20) | 3 182(13) | −2 021(16) | 313(11) |
| Au(3) | 5 015(1) | −977(1) | 2 432(1) | C(21) | 2 751(13) | −1 365(12) | 364(10) |
| Nb(1) | 5 434(1) | 2 648(1) | 3 150(1) | C(22) | 1 518(16) | 99(14) | 663(15) |
| Nb(2) | 2 765(1) | −1 816(1) | 1 757(1) | C(23) | −79(18) | −1 727(17) | 979(17) |
| Nb(3) | 7 219(1) | −372(1) | 2 818(1) | C(24) | −6(13) | −1 896(13) | −928(12) |
| Si(1) | 7 919(3) | 4 103(3) | 2 648(3) | C(25) | 2 249(12) | −3 040(11) | 2 538(11) |
| Si(2) | 3 087(3) | 2 526(3) | 3 942(3) | C(26) | 3 078(13) | −2 144(12) | 3 198(11) |
| Si(3) | 791(4) | −1 343(4) | 297(4) | C(27) | 2 830(15) | −1 330(12) | 3 349(11) |
| Si(4) | 2 104(4) | −4 352(3) | 2 224(4) | C(28) | 1 839(14) | −1 667(13) | 2 826(13) |
| Si(5) | 6 276(4) | −2 982(3) | 974(4) | C(29) | 1 475(12) | −2 703(11) | 2 345(12) |
| Si(6) | 9 262(3) | 1 934(3) | 4 806(3) | C(30) | 1 530(13) | −4 946(13) | 3 041(12) |
| C(1) | 6 537(11) | 3 534(10) | 2 373(10) | C(31) | 1 263(17) | −5 135(16) | 1 033(15) |
| C(2) | 5 888(14) | 4 018(12) | 2 580(11) | C(32) | 3 359(16) | −4 325(17) | 2 325(17) |
| C(3) | 4 888(13) | 3 390(16) | 2 095(13) | C(33) | 7 008(12) | −1 586(10) | 1 406(10) |
| C(4) | 4 860(17) | 2 476(14) | 1 552(11) | C(34) | 8 072(12) | −1 040(12) | 1 907(11) |
| C(5) | 5 832(13) | 2 550(13) | 1 695(11) | C(35) | 8 413(15) | 4(12) | 1 947(14) |
| C(6) | 8 326(13) | 5 036(12) | 2 012(12) | C(36) | 7 592(15) | 97(13) | 1 507(11) |
| C(7) | 8 518(13) | 4 793(12) | 3 901(12) | C(37) | 6 730(14) | −819(12) | 1 170(11) |
| C(8) | 8 351(12) | 3 103(11) | 2 250(11) | C(38) | 4 922(13) | −3 324(13) | 450(12) |
| C(9) | 4 437(11) | 2 818(10) | 4 173(10) | C(39) | 6 396(15) | −3 562(14) | 1 878(14) |
| C(10) | 4 957(14) | 2 252(12) | 4 464(10) | C(40) | 6 800(14) | −3 484(14) | 72(13) |
| C(11) | 6 012(12) | 2 851(12) | 4 769(10) | C(41) | 8 300(12) | 592(11) | 4 335(10) |
| C(12) | 6 182(13) | 3 811(12) | 4 681(11) | C(42) | 7 289(11) | 168(13) | 4 396(10) |
| C(13) | 5 251(13) | 3 793(11) | 4 335(10) | C(43) | 6 888(13) | −914(14) | 4 116(12) |
| C(14) | 2 679(15) | 2 985(14) | 2 982(14) | C(44) | 7 646(14) | −1 157(13) | 3 868(12) |
| C(15) | 2 920(12) | 3 224(12) | 5 026(11) | C(45) | 8 483(12) | −240(12) | 3 996(11) |
| C(16) | 2 301(12) | 1 140(11) | 3 612(11) | C(46) | 10 205(13) | 2 062(12) | 5 849(12) |
| C(17) | 1 743(11) | −1 855(11) | 397(11) | C(47) | 9 977(13) | 2 319(12) | 3 974(12) |
| C(18) | 1 575(12) | −2 885(11) | 343(11) | C(48) | 8 615(11) | 2 742(11) | 5 113(11) |

led to the formation of neutral bimetallic RuAu and $RuAu_2$ complexes or a neutral raft cluster with the niobium trihydride. We are presently studying the reactivity of this type of derivative and also attempting the synthesis of dihydrogen bimetallic derivatives.

## Experimental

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry, oxygen-free argon. Solvents were distilled from appropriate drying agents and degassed before use. The complexes $[MH_3(L)L']$ **1–3** were prepared as reported previously.[1a,20] The salt $[Au(PPh_3)]PF_6$ was prepared *in situ* from the reaction of $[Au(PPh_3)Cl]$[21] and $TlPF_6$; $[Au\{N(SiMe_3)_2\}(PPh_3)]$ was prepared as described in the literature.[13] Carbon and hydrogen microanalyses were performed with a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 $cm^{-1}$ using a Perkin-Elmer 599 spectrophotometer. Proton and $^{31}P$ NMR spectra were recorded on Varian FT80A and Bruker WM 250 spectrometers respectively with $SiMe_4$ ($^1H$) and $H_3PO_4$ ($^{31}P$) as standards.

*Preparations.*—$[L(L')M(\mu\text{-}H)_2\{Au(PPh_3)\}_2]PF_6$[M = Ru, L = $\eta$-$C_5Me_5$, L′ = $P(C_6H_{11})_3$, **4**; M = Nb, L = L′ = $\eta$-$C_5H_4SiMe_3$, **5**; *and* M = Nb, L = L′ = $\eta$-$C_5H_3(SiMe_3)_2$, **6**]. A thf solution (3 $cm^3$) of $[Au(PPh_3)]PF_6$ was prepared *in situ* by reaction (30 min) of $[Au(PPh_3)Cl]$ (0.150 g, 0.30 mmol) with $TlPF_6$ (0.110 g, 0.31 mmol). The white precipitate (TlCl) was separated by filtration and the solution was added to a thf solution (15 $cm^3$) of **1** (0.150 g, 0.29 mmol). The mixture was stirred for 1 h to give a yellow solution which was evaporated to dryness to give a yellow residue. Complex **4** was obtained as a yellow microcrystalline solid by crystallization from acetone–diethyl ether (1:1). Yield 0.410 g (90%). Complexes **5** and **6** were obtained in similar yields by use of **2** (0.300 g, 0.81 mmol) or **3** (0.300 g 0.58 mmol) in place of **1**.

**4** (Found: C, 48.3; H, 5.6. Calc. for $C_{64}H_{75}Au_2F_6P_4Ru$: C, 48.6; H, 5.1%). IR (Nujol): ν(Ru–μ-H–Ru), 1710 m (br); $PF_6^-$, 840s (br) $cm^{-1}$. NMR ($[^2H_6]$acetone): $^1H$, δ 7.49 (complex m 30 H, $PPh_3$), 2.12 (s, 15 H, $\eta$-$C_5Me_5$), 2–1 [33 H, $P(C_6H_{11})_3$], −8.6 (AA′XX′Y, 2 H, $J_{P^1H}$ 47, $J_{P^2H}$ 18, μ-H); $^{31}P$-$\{^1H\}$, δ 77.96 [t, $J_{PP}$ 3.1 Hz, $P(C_6H_{11})_3$], 45.5 (d, $PPh_3$).

**5** (Found: C, 43.1; H, 4.1. Calc. for $C_{54}H_{58}Au_2F_6NbP_3Si_2$: C, 43.6; H, 4.15%). IR (Nujol): $SiMe_3$, 1250s; $PF_6^-$, 840s (br) $cm^{-1}$. $^1H$ NMR ($[^2H_6]$acetone): δ 7.9–7.2 (complex m, 30 H, $PPh_3$); 5.76 (AA′BB′, 8 H, $J_{HH}$ 2, $C_5H_4$); 0.28 (s, 18 H, $SiMe_3$); −3.81 (AA′XX′, 2 H, $J_{P^1H}$ 39, $J_{P^2H}$ 7.5 Hz, μ-H).

**6** (Found: C, 44.3; H, 4.8. Calc. for $C_{58}H_{74}Au_2F_6NbP_3Si_4$: C, 44.2; H, 4.7%). IR (Nujol): $SiMe_3$, 1250; $PF_6^-$, 840s (br). $^1H$ NMR ($[^2H_6]$acetone: δ 7.7–7.3 (complex m, 30 H, $PPh_3$); 5.48 (br, 6 H, $C_5H_3$); 0.37 (s, 36 H, $SiMe_3$); −3.85 (AA′XX′, 2 H, $J_{P^1H}$ 42, $J_{P^2H}$ 7 Hz).

$[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)_2Au(PPh_3)]$ **7**. A toluene solution (15 $cm^3$) of **1** (0.150 g, 0.29 mmol) was added to a toluene solution (15 $cm^3$) of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ (0.190 g, 0.31 mmol). After stirring at room temperature for 1 h the solvent was pumped off and the residue extracted with hexane. Complex **7** was obtained on partial evaporation and cooling as a yellow microcrystalline solid. Yield: 0.170 g (60%) (Found: C, 55.9; H, 7.0. Calc. for $C_{46}H_{64}AuP_2Ru$: C, 56.5; H, 6.6%). IR (Nujol): ν(Ru–μ-H–Ru), 1730m (br) $cm^{-1}$. NMR ($[^2H_6]$-benzene): $^1H$, δ 8–7 (complex m, 15 H, $PPh_3$); 2.40 (s, 15 H, $\eta$-$C_5Me_5$), 2.2–1.2 [complex m, 33 H, $P(C_6H_{11})_3$]; −9.20 (dd, 2 H, $J_{P^1H}$ 40.9, $J_{P^2H}$ 25 Hz); $^{31}P$-$\{^1H\}$, δ 80.7 [s, $P(C_6H_{11})_3$]; 47.6 (s, $PPh_3$).

$[(\eta\text{-}C_5Me_5)\{(C_6H_{11})_3P\}Ru(\mu\text{-}H)\{Au(PPh_3)\}_2]$ **8**. A toluene solution (15 $cm^3$) of **1** (0.150 g, 0.29 mmol) was added to a toluene solution (10 $cm^3$) of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ (0.380 g, 0.61 mmol). After stirring for 1 h, the reaction mixture was worked up as for **7**. Complex **8** was obtained as an orange microcrystalline solid. Yield: 0.300 g (73%) (Found: C, 53.0; H, 5.7. Calc. for $C_{64}H_{80}Au_2P_3Ru$: C, 53.4; H, 5.5%). IR (Nujol): ν(Ru–μ-H–Ru), 1620m (br) $cm^{-1}$. NMR ($[^2H_6]$benzene): $^1H$, δ

8–7 (complex m, 30 H, $PPh_3$); 2.65 (s, 15 H, η-$C_5Me_5$), 2.2–1.2 [complex m, 33 H, $P(C_6H_{11})_3$]; −10 (ddd, 1 H, $J_{P^1H}$ 28, $J_{P^2H}$ 33, $J_{P^3H}$ 4 Hz); $^{31}P$-{$^1H$}, δ 79 [$J_{PP}$ 17, $P(C_6H_{11})_3$]; 42 ($J_{PP}$ 21, Ru–μ-H–Au$PPh_3$); 37.5 (Ru–Au$PPh_3$).

$[Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6]$ **9**. To a toluene solution (25 $cm^3$) of **2** (0.250 g, 0.68 mmol) was added a solution of $[Au\{N(SiMe_3)_2\}(PPh_3)]$ (0.440 g, 0.71 mmol) in toluene (10 $cm^3$). A rapid colour change was observed and after stirring for 1 h a deep purple solution was obtained which was concentrated under vacuum and then cooled to give purple needles of **9**. Yield: 0.460 g (60%) (Found: C, 34.6; H, 4.9. Calc. for $C_{48}H_{84}Au_3Nb_3Si_6$: C, 33.9; H, 4.9%). IR (Nujol): $SiMe_3$, 1246s $cm^{-1}$. $^1H$ NMR ($[^2H_6]$benzene): δ 5.02 (AA'BB', 24 H, $J_{HH}$ 2 Hz, $C_5H_4$); 0.31 (s, 54 H, $SiMe_3$); −2.90 (s, 6 H, hydrides).

*Crystal Structure Determination of Complex* **9**.—*Crystal data.* $C_{48}H_{84}Au_3Nb_3Si_6$, $M$ = 1699.326, triclinic, space group $P\bar{1}$, $a$ = 14.927(2), $b$ = 15.083(2), $c$ = 15.632(2) Å, α = 103.81(1), β = 99.20(1), γ = 112.55(1)°, $U$ = 3029.8(8) $Å^3$ (by least-squares refinement of the 2θ values in the range 20–32° of 50 accurately measured reflections), $Z$ = 2, $D_c$ = 1.863 g $cm^{-3}$, λ = 0.710 69 Å, $F(000)$ = 1632 and μ(Mo-Kα) = 78.94 $cm^{-1}$; crystal dimensions 0.06 × 0.12 × 0.61 mm (sealed in a capillary).

*Data collection and processing.* Siemens AED diffractometer, ω–2θ mode, graphite monochromatized Mo-Kα radiation; a total of 8341 reflections ($\pm h$, $\pm k$, $+l$; $3 \leqslant 2\theta \leqslant 45°$) were measured. Of 7065 independent reflections, 4451 having $I > 2\sigma(I)$ were considered observed and used in the analysis. Data were corrected for Lorentz and polarization effects, and for absorption (ψ-scan method from 10 reflections),[22] with min. and max. transmission factors 0.2678 and 0.3813 respectively.

*Structure solution and refinement.* The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, except the carbons of the methyl groups. Hydrogen atoms (except hydrides) were placed at idealized positions riding upon their respective carbon atoms and included in the last cycles of refinement. The final values of the agreement indices were $R$ = 0.038 and $R'$ = 0.036. The SHELX system of computer programs was used.[23] Atomic scattering factors, corrected for anomalous dispersion of Au, Nb and Si, were taken from ref. 24. Final atomic coordinates for the non-hydrogen atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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## References

1 (*a*) A. Antiñolo, B. Chaudret, G. Commenges, M. Fajardo, F. Jalón, R. H. Morris, A. Otero and C. T. Schweltzer, *J. Chem. Soc., Chem. Commun.*, 1988, 1210; (*b*) T. Arliguie, B. Chaudret, J. Devillers and R. Poilblanc, *C. R. Acad. Sci., Ser. II*, 1987, **305**, 1523, (*c*) T. Arliguie, C. Border, B. Chaudret, J. Devillers and R. Poilblanc, *Organometallics*, 1989, **8**, 1308.
2 D. H. Jones, L. A. Labinger and D. P. Weitekamp, *J. Am. Chem. Soc.*, 1989, **111**, 3087, K. W. Zilm, D. M. Heinekey, J. M. Millar, N. G. Payne, S. P. Neshyba, J. C. Duchamp and J. Szczyrba, *J. Am. Chem. Soc.*, 1990, **112**, 920, K. W. Zilm, D. M. Heinekey, J. M. Millar, N. G. Payne and P. Demou, *J. Am. Chem. Soc.*, 1989, **111**, 3088.
3 B. Chaudret, G. Commenges, F. Jalón and A. Otero, *J. Chem. Soc., Chem. Commun.*, 1989, 210.
4 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.
5 See: A. M. Mueting, W. Bos, B. D. Alexander, P. D. Boyle, J. A. Casalnuovo, S. Balaban, L. N. Ito, S. M. Johnson and L. H. Pignolet, *New. J. Chem.*, 1988, **12**, 505.
6 A. Antiñolo, J. K. Burdett, B. Chaudret, O. Eisestein, M. Fajardo, F. Jalón, F. Lahoz, J. A. López and A. Otero, *J. Chem. Soc., Chem. Commun.*, 1990, 17.
7 T. Arliguie, B. Chaudret, F. Jalón and F. Lahoz, *J. Chem. Soc., Chem. Commun.*, 1988, 998.
8 B. D. Alexander, B. J. Johnson, S. M. Johnson, A. L. Casalnuovo and L. H. Pignolet, *J. Am. Chem. Soc.*, 1986, **108**, 4409.
9 M. Fajardo, M. P. Gómez-Sal, P. Royo, S. Martínez-Carrera and S. García-Blanco, *J. Organomet. Chem.*, 1986, **312**, C44.
10 H. P. Fritz, *Adv. Organomet. Chem.*, 1964, **1**, 239.
11 H. Burger, *Organomet. Chem. Rev. A*, 1968, **3**, 425.
12 A. Antiñolo, S. García-Lledó, J. Martinez de llarduya and A. Otero, *J. Organomet. Chem.*, 1987, **335**, 85 and refs. therein.
13 A. Shiotani and H. Schmidbaur, *J. Am. Chem. Soc.*, 1970, **92**, 7003.
14 B. R. Sutherland, K. Folting, W. E. Streib, D. M. Ho, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1987, **109**, 3489.
15 B. D. Alexander, B. J. Johnson, S. M. Johnson, P. D. Boyle, N. C. Kann, A. M. Mueting and L. H. Pignolet, *Inorg. Chem.*, 1987, **26**, 3506.
16 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126.
17 F. A. Cotton and R. L. Luck, *Inorg. Chem.*, 1989, **28**, 6.
18 (*a*) J. J. Goudsmit, J. G. Jeffrey, B. F. G. Johnson, J. Lewis, R. C. S. McQueen, A. J. Sanders and J. C. Liu, *J. Chem. Soc., Chem. Commun.*, 1986, **24**; (*b*) G. Longani, M. Manassero and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 7973; (*c*) B. R. Sutherland, D. M. Ho, J. C. Huffman and K. G. Caulton, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 134; (*d*) T. H. Lemmen, J. C. Huffman and K. G. Caulton, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 262; (*e*) L. F. Rhodes, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1983, **105**, 5137; (*f*) F. Bachechi, J. Ott and L. M. Venanzi, *J. Am. Chem. Soc.*, 1985, **107**, 1760.
19 F. Calderazzo, G. Pampaloni, U. Englert and J. Strähle, *J. Organomet. Chem.*, 1990, **383**, 45; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 471.
20 T. Arliguie and B. Chaudret, *J. Chem. Soc., Chem. Commun.*, 1986, 985; T. Arliguie, C. Border, B. Chaudret, J. Devillers and R. Poilblanc, *Organometallics*, 1989, **8**, 1308; H. Suzuki, D. H. Lee, N. Oshima and Y. Moro-Oka, *Organometallics*, 1987, **6**, 1569.
21 M. I. Bruce, B. K. Nicholson and O. Bin Shawkataly, *Inorg. Synth.*, 1989, **26**, 325.
22 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
23 G. M. Sheldrick, SHELX Program for crystal structure determination, University of Cambridge, 1976.
24 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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