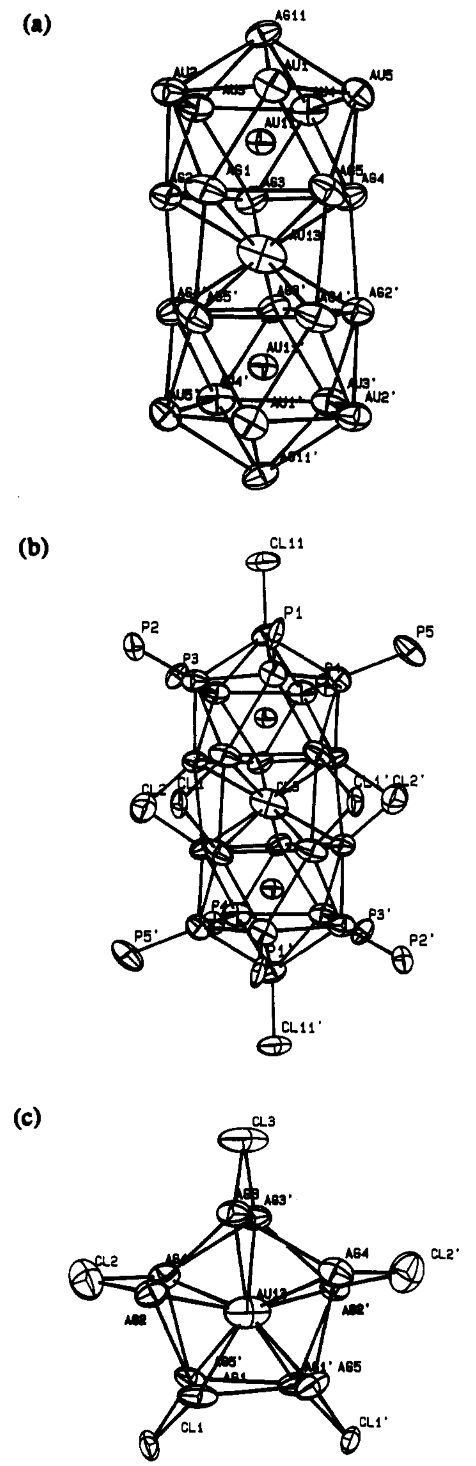

Figure 1. Molecular architecture of the 25-metal-atom cluster $[(p\text{-Tol}_3P)_{10}Au_{13}Ag_{12}Cl_7]^{2+}$ (**2**) as the $(SbF_6)^-$ salt: (a) the metal core, $Au_{13}Ag_{12}$; (b) the metal–ligand framework, $P_{10}Au_{13}Ag_{12}Cl_7$; (c) projection of the two silver pentagons and the five doubly bridging chloride ligands along the idealized 5-fold axis (which passes through Ag11, Au11, Au13, Au11′, and Ag11′). Atoms related by the crystallographic 2-fold (C_2-2) symmetry are designated as primes. All radial bonds (12 each) from Au11 and Au11′ have been omitted for clarity. All molecular parameters are normal. The importance distances are as follows (n = 1–5): Au11–Au(n) = 2.749 (av) Å, Au11–Ag(n) = 2.816 (av) Å, Au11–Ag11 = 2.743 (9) Å, Au11–Au13 = 2.813 (5) Å, Au13–Ag(n) = 2.881 (av) Å; intrapentagonal, Au(n)–Au(n + 1) = 2.914 (av) Å, Ag(n)–Ag(n + 1) = 2.912 (av) Å; interpentagonal, Au(n)–Ag(n or n – 1) = 2.885 (av) Å, Ag1–Ag5′ = 3.04 (1) Å, Ag2–Ag4′ = 2.94 (1) Å, Ag3–Ag3′ = 2.92 (1) Å, Au–P = 2.35 (av) Å, Ag11–Cl11 = 2.43(3) Å, Ag(n)–Cl(n) = 2.44 (av) Å. The five doubly bridging chloride ligands form a distorted pentagon with nonbonding (crystallographically independent) distances of Cl1···Cl1′ = 5.34 Å, Cl1···Cl2 = 4.69 Å, and Cl2···Cl3 = 5.53 Å.

The relative orientation of the four metal pentagons can be described as ABAB (sss) for **1** and ABBA (ses) for **2**, respectively. The corresponding orientation of the *two* icosahedra may be described as $\alpha(\beta)\alpha$ and $\alpha(\gamma)\beta$, respectively. The former has an "additional" icosahedron (whose orientation is in parentheses) in the middle due to the staggered arrangement of the two middle rings in the sss configuration. The latter produces a bicapped pentagonal prism whose orientation is designated as γ (in parentheses). The *propagation* of icosahedra via vertex, edge, or face sharing through space is critically dependent upon the relative orientation of the icosahedral units (the building blocks) and is of current interest in terms of the structures of quasicrystals[14] and amorphous materials.[15]

Finally, we note that the ses metal configuration (as observed for **2**) allows stereochemically a "polyicosahedral" growth pathway via vertex sharing to give bi-, tri-, and tetraicosahedral supraclusters as exemplified by the structurally characterized 25- (**2**), 37- (**3**)[7] or 38- (**4**),[8] and 46- (**5**)[9] metal-atom Au–Ag clusters, respectively. In all these structures, the icosahedral units are linked by (interpenetrating) bicapped pentagonal prisms (γ), instead of the (interpenetrating) icosahedra (β) as observed in the 25-metal-atom cluster **1**[6a] with an sss metal configuration.

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Supplementary Material Available: Full listings of complete structural data (Table I), positional parameters (Table II), anisotropic thermal parameters (Table III), positional and orientational parameters of 15 tolyl groups (Table IV), interatomic distances (Table V), interatomic angles (Table VI), and details of the preparation and crystallization (Table VII) for the title compound (20 pages); a listing of observed and calculated structure factors (Table VIII) (61 pages). Ordering information is given on any current masthead page.

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Short Spin–Lattice Relaxation Times of Hydride Ligands. Proton–Metal Dipole–Dipole Interactions

T_1 measurements have recently been used for obtaining structural information about metal hydride complexes.[1–3] Crabtree and Luo[4] have recently tested the basis of the T_1 method, assuming that only proton–proton dipole–dipole interactions (HHDDI) dominates the relaxation. They have found that, for a series of mononuclear polyhydrides for which both structural and relaxation data are available, there was good agreement between the calculated and observed $T_{1\,\min}$ values.

This agreement is rather surprising in the case of rhenium hydrides, where significant metal–H dipole–dipole interactions (MHDDI) can be expected. Indeed, with $r_{\text{Re-H}} = 1.7$ Å and $\tau_c = 0.62/2\pi\nu$[5] at 250 MHz, the well-known[6] eq 1 (where C =

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Table I. NMR Data for Complexes I–III

parameter	I ($C_6D_5CD_3$)	II ($(CD_3)_2CO$)	III ($C_6D_5CD_3$)
δ(CoH), ppm	−14.95 (290 K)	−13.13 (240 K)	−12.09 (290 K)
$J(^1HCo^{31}P)$, Hz	23.5	±55(cis), ±35(cis), ∓75(trans)[a]	48.5
δ(Ph), ppm	7.45 (o), 7.00 (m, p) (290 K)	7.30[b] (240 K)	7.36 (o), 6.90 (m, p) (290 K)
$\delta(^{31}P)$, ppm	72.03 (270 K), 74.75 and 70.62 (160 K)[c]	79.0 and 67.5 (180–290 K)	55.8 (290–180 K)
$T_{1\,\mathrm{min}}$(CoH), ms	40 (225 K)	43 (220 K)	41 (225 K)
$T_{1\,\mathrm{min}}$(Ph–H), ms	390 (o), 720 (m, p) (225 K)		490 (o), 730 (m, p) (225 K)

[a] The values were obtained by a simulation of the CoH_2 signal as XX′—part of the AA′BB′XX′ spin system (A,B = ^{31}P, X = ^1H). [b] The center of the multiplet. [c] The signals have equal intensities; $\Delta G^{\ddagger}$, the value for the position exchange process, is calculated as 7.5 kcal/mol at 170 K.

$(4/30)r_{M-H}^{-6}\gamma_H^2\gamma_M^2\hbar^2I(I+1)$, I = the spin of M, ω_H, ω_M ($\omega = 2\pi\nu$) = the Larmor frequencies of the nuclei ^1H and M, and τ_c = the molecular correlation time) gives $1/T_1 = 3.8$ s^{-1}. Hence, between 22 and 27% of the hydride relaxation may come from the MHDDI in classical rhenium hydrides, where $1/T_{1\,\mathrm{min}}$ values of 15–18.8 s^{-1} are actually observed.[2]

$$1/T_1 = C[3\tau_c/(1+\omega_H^2\tau_c^2) + 6\tau_c/(1+(\omega_H+\omega_M)^2\tau_c^2) + \tau_c/(1+(\omega_H-\omega_M)^2\tau_c^2)] \quad (1)$$

Equation 1 suggests that the M–H dipolar mechanism, in addition to the H–H dipolar one, can be appreciable in hydride complexes of ^{51}V ($I = {}^7/_2$), ^{55}Mn ($I = {}^5/_2$),[7] ^{59}Co ($I = {}^7/_2$), and ^{93}Nb ($I = {}^9/_2$). We decided to obtain $T_{1\,\mathrm{min}}$ values for the known complexes of cobalt $CoH(Ph_2PCH_2CH_2PPh_2)_2$ (I), $[CoH_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ (II), and $CoH(CO)(PPh_3)_3$ (III), where a M–H dipolar relaxation of the hydride ligands should be potentially more efficient than in rhenium hydrides.

The complexes were prepared by literature methods: $CoH(Ph_2PCH_2CH_2PPh_2)_2$,[8,9] $[CoH_2(Ph_2PCH_2CH_2PPh_2)_2]^+[BF_4]^-$,[9] and $CoH(CO)(PPh_3)_3$.[10] Solutions of the hydrides were carefully degassed and sealed under an Ar atmosphere in 5-mm NMR tubes. The T_1 experiments were performed on a 200-MHz Bruker instrument with a standard 180°–τ–90° pulse sequence.

A summary of the $^1H\{^{31}P\}$ NMR data for complexes I–III is given in Table I. The X-ray data for $CoH(Ph_2P(CH_2)_3PPh_2)_2$[11] (IV) indicate that the geometry of IV is that of a distorted trigonal bipyramid. For I this is also evident from the $^{31}P\{^1H\}$ NMR spectra, where two broad signals of equal intensity are observed at low temperatures. Our $^1H\{^{31}P\}$ NMR data for II support the formulation of the complex, based on IR measurements,[9] as an octahedral *cis*-dihydride.

It should be noted that we attempted to prepare $[CoH_2(CO)(PPh_3)_3]^+$. However, a protonation of the monohydride III in CD_2Cl_2 or THF-d_8 with HBF_4 or $HClO_4$ was accompanied by isolation of dihydrogen. A 1:1:1 triplet of HD (δ 4.5, J_{HD} = 43.2 Hz) also appeared in the ^1H NMR spectrum when III was treated by CF_3COOD in toluene-d_8. Hence, the dihydride $[CoH_2(CO)(PPh_3)_3]^+$ is probably unstable in solution.

Table I gives the $T_{1\,\mathrm{min}}$ values for the hydrogen nuclei in complexes I–III. The relaxation of the phenyl protons ($T_{1\,\mathrm{min}}$ = 0.4–0.7 s at 225 K) was dominated by their mutual dipole interactions, so similar $T_{1\,\mathrm{min}}$ values were observed for the phosphine protons of $RuH_4(PPh_3)_2$,[12] $RuH_2(CO)(PPh_3)_3$,[12] and $PtHCl(PPh_3)_2$.[13] However, metal-bonded hydrogen atoms in complexes I–III relax significantly faster ($T_{1\,\mathrm{min}}$ = 0.040–0.043 s)[14] than in complexes where the main contribution to the relaxation of hydride ligands probably comes from dipolar interactions with phosphine ^1H and ^{31}P nuclei.[3,4] For example, $T_{1\,\mathrm{min}}$ values for ^1H NMR hydride resonance(s) are equal to 0.38 s in $PtHCl(PPh_3)_2$,[13] 0.2 s in $IrHCl_2(P(Pr^i)_3)_2$,[15] 0.26 s in $RhHCl_2(P(Pr^i)_3)_2$,[16] and 0.18–0.20 s in $RuH_2(CO)(PPh_3)_3$[12] at 200 MHz. It is doubtful that a relaxation rate of hydride ligands can be more than 5 s^{-1} (at 200 MHz) if there are not significant dipole interactions between H ligands (or between metal and hydrogen atoms).

Table II. Calculated Minimum ^1H T_1 Times Corresponding to Different Co–H Distances

r(Co–H), Å	1.4	1.45	1.5	1.55	1.6
$T_{1\,\mathrm{min}}$(Co–H), ms	31	39	47.5	58	70
$T_{1\,\mathrm{min}}$, ms	29–27	35–32	42–38	49–45	58–52

The contribution to the relaxation rate of proton, due to the MHDDI, is given by eq 1. If we assume that τ_c in the minimum is 7.36×10^{-10} s (ν = 200 MHz, $\tau_c = 0.93/2\pi\nu$), we can in principle calculate $T_{1\,\mathrm{min}}$(Co–H) from eq 1 with r_{Co-H} = 1.4–1.6 Å. Table II lists some calculated $T_{1\,\mathrm{min}}$(Co–H) contributions to total $T_{1\,\mathrm{min}}$ times, obtained from eq 2 with other sources of relaxation being taken into account. We believe that reasonable values of $1/T^*_{1\,\mathrm{min}}$ can be equal to 3–5 s^{-1} at 200 MHz.

$$1/T_{1\,\mathrm{min}} = 1/T_{1\,\mathrm{min}}(\text{Co–H}) + 1/T^*_{1\,\mathrm{min}} \quad (2)$$

The agreement between the calculated and the experimental $T_{1\,\mathrm{min}}$ values is observed if r_{Co-H} is ca. 1.5 Å. Monohydrides III and IV have the Co–H distances of 1.41 (9) Å[10] and 1.42 (3) Å,[11] respectively, according to X-ray diffraction. However, because the position of a proton and the centroid of electron density associated with it for a hydrogen atom bound to another atom do not coincide, the observed disparity is typical for a M–H bond.[17]

^{93}Nb has spin $I = {}^9/_2$. In this case still larger relaxation rates are expected. So eq 1 predicts the $T_{1\,\mathrm{min}}$(Nb–H) value of 0.028 s for niobium-bonded hydrogen if r_{Nb-H} = 1.5 Å at 200 MHz.

As was shown above, MHDDI contribute markedly to the T_1 relaxation of hydride ligands in rhenium complexes. Cotton and co-workers[17] have recently confirmed that this fact in the case of Cp_2ReH. Unfortunately, they have given a qualitative interpretation of the experimental data only. Therefore we decided to recalculate the $T_{1\,\mathrm{min}}$ value for the binuclear complex $Re_2H_4(\mu\text{-}H)_4(PEt_2Ph)_4$. In this polyhydride both the neutron diffraction structure[18] and the $T_{1\,\mathrm{min}}$ value[17] are available, but the observed $T_{1\,\mathrm{min}}$ of 140 ms at 400 MHz is significantly shorter than that calculated by Crabtree and Luo[4] (302 ms).

The known equation for HHDDI[2] and eq 1 applied to the structural data for $Re_2H_4(\mu\text{-}H)_4(PEt_2Ph)_4$ give $1/T_{1\,\mathrm{min}}$ of 3.2 and 2.65 s^{-1}, respectively ($\tau_c = 0.62/2\pi\nu$, ν = 400 MHz), and the total

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(5) This τ_c holds at the maximum of the rate of HHDDI relaxation. Actually, at the maximum of the function given by eq 1, τ_c is equal to $0.93/2\pi\nu$. With this τ_c value, eq 1 gives $1/T_1$ = 4.1 s^{-1}. Thus, the difference in these τ_c values leads to the 7% difference in $1/T_1$ values and can be neglected in the case of semiquantitative analysis.

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$T_{1\,\mathrm{min}}$ value is equal to 171 ms. The difference (1.3 s^{-1}) between the calculated rate and the observed one is probably due to a contribution to the relaxation of hydride ligands from the phosphine protons and the deuterons of the solvent molecules.[3,7] For example, in the complex $Re_2H_4(\mu\text{-}H)_4(PMe_3)_4$, there are few phosphine protons and the averaged $T_{1\,\mathrm{min}}$ of H ligands is 162 ms.[17]

Thus, a MHDD interaction can significantly decrease ^1H T_1 relaxation times. For this reason one should be very careful with quantitative interpretation of the T_1 data in the case of hydride complexes of V, Mn, Co, Nb, and Re.[19a]

Note Added in Proof. An analysis of the factors contributing to the spin–lattice relaxation time T_1 for $OsH_4(P(Tol)_3)_3$ and related hydrides, including, among other things, the large metal–hydride dipole–dipole interaction contributing to a short $T_{1\,\mathrm{min}}$ in $Re_2H_8(PEt_2Ph)_4$, appeared after this work was entered into production (see: Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173-4184).

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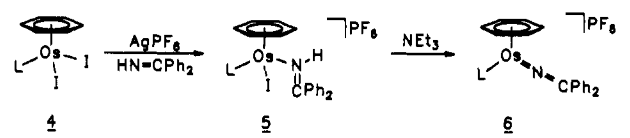
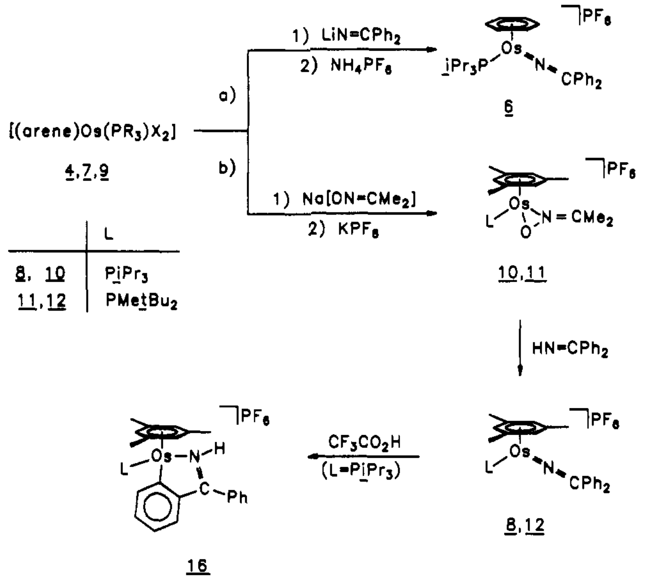
New Synthetic Routes to Azavinylidene Half-Sandwich Type Complexes

Among transition-metal complexes containing metal–nitrogen double bonds, nitrene–metal as well as azavinylidene–metal compounds have received increasing attention.[1,2] In connection with our studies on vinylidene–metal derivatives of the general type [(ring)M(=C=CRR′)(L)],[3,4] we recently found that the corresponding *azavinylidene* complexes $[(C_6H_6)Os({=}N{=}CRR')P(Me)(t\text{-}Bu)_2]PF_6$ (**3**) are accessible from $[(C_6H_6)OsH(I)P(Me)(t\text{-}Bu)_2]$ (**1**), $AgPF_6$, and ketoximes in good yields.[5] In two cases, the cationic hydrido oxime derivatives $\{(C_6H_6)OsH[N(OH){=}CRR']P(Me)(t\text{-}Bu)_2\}PF_6$ (**2**) have been characterized as intermediates which by elimination of water give the final products.

Scheme I. L = P-i-Pr$_3$



Scheme II



During attempts to prepare analogues of **3** with ligands L other than $P(Me)(t\text{-}Bu)_2$, we observed that the type of phosphine ligand used plays a critical role in the course of the reaction. Replacement of $P(Me)(t\text{-}Bu)_2$ even by P-*i*-Pr$_3$ causes difficulties that were unexpected owing to the similar size of the two phosphine molecules.[6]

In trying to escape the dilemma, we discovered that ketimines are more suitable starting materials for the synthesis of azavinylidene–osmium complexes [(arene)Os(=N=CRR′)(L)]X than ketoximes. Here we describe three alternative pathways to prepare compounds of the above-mentioned type and in addition report the synthesis of the first azavinylidene–*iridium* complex containing $[(C_5Me_5)IrP(Me)(t\text{-}Bu)_2]$ as a structural unit.

Under conditions similar to those used for the preparation of **3**, compound **4**[7] reacts with HN=CPh$_2$ in presence of $AgPF_6$ to give the orange-yellow imine complex **5** (see Scheme I).[8] If after filtration the reaction mixture is treated with NEt_3, orange crystals of the azavinylidene complex **6** are isolated in 78% yield.[9] A similar procedure has also been applied for the preparation of the corresponding mesitylene–osmium derivative $[(mes)Os({=}N{=}CPh_2)(P\text{-}i\text{-}Pr_3)]PF_6$ (**8**),[9] in this case using $[(mes)Os(P\text{-}i\text{-}Pr_3)Cl_2]$

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(8) Selected IR and NMR spectroscopic data of **5** are as follows. IR (KBr): ν(NH) 3235 cm^{-1}. ^1H NMR (60 MHz, CD_3NO_2): δ 10.93 (s, br, 1 H, NH), 7.6 (m, 10 H, C_6H_5), 5.77 (s, 6 H, C_6H_6), 2.90 (m, 3 H, $PCHCH_3$), 1.33 (dd, 18 H, J(PH) = 13.7 Hz J(HH) = 7.1 Hz, $PCHCH_3$). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ −1.74 (s, P-*i*-Pr$_3$), −145.48 (sept, J(PF) = 707.4 Hz, PF_6).

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