$(PPh_3)NO_3$. Only one isomer was observed in solution with a structure which is presumably analogous to that of **2** (see Experimental Section). The ^{31}P NMR spectrum displayed three multiplets, δ 45.3 (t, J = 31 Hz) assigned to $AuPPh_3$, δ 157.3 (t of d, J = 53 and 31 Hz) assigned to the cis $RuP(OMe)_3$ ligands, and δ 149.6 (t, J = 53 Hz) assigned to the trans $RuP(OMe)_3$ ligands. This assignment was based on comparison to $[AuRu(H)_2(dppm)_2(PPh_3)]^+$ and ^1H NMR with selective ^{31}P decoupling (see Experimental Section). The addition of 6 equiv of PPh_3 in CH_2Cl_2 at room temperature showed evidence of fast exchange between the $AuPPh_3$ ligand and free PPh_3, since the $AuPPh_3$ resonance at δ 45.3 was gone and the free PPh_3 resonance at δ −1.5 was very broad. Also, the $RuP(OMe)_3$ resonances were simplified to two triplets as a result of the loss of $AuPPh_3$ coupling. There was also evidence for cleavage of the Ru–Au bond and $(AuPPh_3)^+$ ion extrusion due to the presence of a small amount of $H_2Ru[P(OMe)_3]_4$. However, the reaction did not occur to a significant extent even over a period of 2 weeks at room temperature.

It is not readily apparent why some of these clusters were susceptible to the extrusion of gold by reaction with PPh_3 while others were not. It most likely has to do with the coordination environment of the transition metal. The number, basicity, and position of the phosphine and other ligands on the transition metal are important factors, but this is not clear as yet. Notwithstanding this, the addition of 1 equiv or more of PPh_3 is indeed a very useful way, although not entirely ubiquitous, of making new transition-metal–gold phosphine clusters.

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Registry No. **1**, 108969-20-6; **2**, 108969-22-8; **3**, 108969-24-0; **4**, 108969-26-2; $[AuIr(H)_2(bpy)(PPh_3)_2(CH_3CN)](BF_4)_2$, 108969-28-4; $\{Au_5Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_5\}(PF_6)_2$, 107742-34-7; $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2](PF_6)_2$, 107712-45-8; $[Au_2Ir(H)(PPh_3)_4(NO_3)](BF_4)$, 93895-71-7; $H_2Ru[P(OMe)_3]_4$, 38784-31-5; $Au(PPh_3)NO_3$, 14897-32-6; $[Ir(H)_2(bpy)(PPh_3)_2]BF_4$, 102538-90-9; $Au(CH_3CN)_2BF_4$, 100333-93-5; $[Au_4Ir(H)_2(PPh_3)_6]BF_4$, 96705-41-8; $[Au_3Rh(H)(CO)(PPh_3)_5]PF_6$, 99595-16-1; $[Au_6Pt(PPh_3)_7](BPh_4)_2$, 107712-39-0; $[AuIr(H)(CO)(PPh_3)_4]PF_6$, 102538-86-3; $IrH(CO)(PPh_3)_3$, 17250-25-8; $[Au(PPh_3)_2]^+$, 47807-21-6; Re, 7440-15-5; Ir, 7439-88-5; Ru, 7440-18-8; PPh_3, 603-35-0; Au, 7440-57-5.

Supplementary Material Available: Tables of final atom positional and thermal parameters, all bond distances and angles in the cation, general temperature factor expressions, least-squares planes, and torsional angles for **1** and a figure showing the ORTEP representation of the cation with labeling scheme (12 pages); a table of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Notes

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^{1}H NMR Spin-Lattice Relaxation Studies of Hydridometal Clusters of Ruthenium and Osmium

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Although it is well established that spin–lattice relaxation times represent a powerful tool in the study of molecular dynamics and solution structures,[1] little attention has been devoted to the use of this parameter in the NMR applications to inorganic and organometallic systems.

Recently Crabtree and co-workers[2] have measured the proton relaxation times T_1 in a series of four mononuclear metal hydrido complexes showing that they are quite short (and invariably shorter than those for the other ^{1}H nuclei present in the compounds studied). These observations prompted us to report our results obtained on some hydrido carbonyl clusters of ruthenium and osmium (see Figure 1 and Table I); it will be also shown that the comparison of the relaxation behavior of different isotopomers may provide an extimate of the internuclear distances involving the hydrides.

To a first approximation, the observed values can be understood simply in terms of two parameters: proximity of other ^{1}H nuclei and molecular mobility (since, within the extreme narrowing situation, T_1 decreases as the molecular dimension increases and/or the temperature is lowered). On this basis it is likely that the spin–lattice relaxation times T_1 of the hydrido ligands are mainly determined by the efficient dipolar interactions with other nearby ^{1}H nuclei in the same molecule; intermoleuclar dipolar contributions seem not to be important. In the dihydrido species (**3**, **8**, **9**) we did not observe any significant difference in T_1 values for different hydride resonances in the same molecule. On the other hand, the large value observed for the sole hydride in **7**, which clearly depends on the long distance from the protons of the organic ligand, is noteworthy; an indirect location of this hydride by X-ray diffraction[3] indicates that it is bridging a

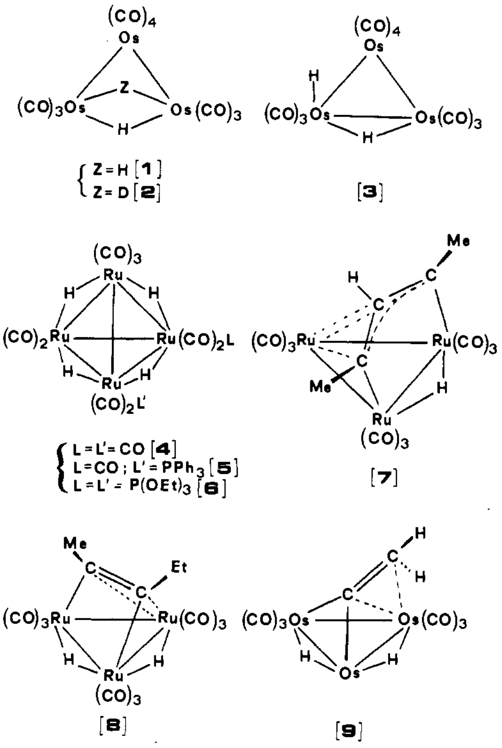

Figure 1. Structures of the hydrido clusters 1–9.

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Table I. T_1 Values of Hydrido Ligands in the Compounds Studied

compd	no.	T_1, s	temp, °C
$H_2Os_3(CO)_{10}$	**1**	6.5	+20
		1.0	−60
$HDO_3(CO)_{10}$	**2**	30.2	+20
$H_2Os_3(CO)_{11}$	**3**	0.9 (terminal)	−60
		0.9 (bridging)	−60
$H_4Ru_4(CO)_{12}$	**4**	4.8	+20
		1.4	−30
$H_4Ru_4(CO)_{11}PPh_3$	**5**	1.6	+20
		0.8	−30
$H_4Ru_4(CO)_9[P(OEt)_3]_3$	**6**	1.2	+20
$HRu_3(CO)_9(MeCCHCMe)$	**7**	24.1	+20
$H_2Ru_3(CO)_9(MeC{=}CEt)$	**8**	1.0	−60
$H_2Os_3(CO)_9(C{=}CH_2)$	**9**	4.3	+20

metal–metal site below the Ru_3 triangle opposite to the σ/π-bonded allylic chain.

In principle, if T_1^{DD} between two ^1H nuclei can be accurately determined (through measurement of the nuclear overhauser enhancement when the two ^1H nuclei resonate at different frequencies) and the molecular correlation time τ_c is known by an independent experiment, ^1H-T_1 can provide a method to evaluate the internuclear distance between the two interacting nuclei. However when the dipolar interaction involves two magnetically equivalent nuclei as in **1**, T_1^{DD} can be obtained by a different approach. This consists in measuring the ^1H-T_1 of the monodeuteriated species $HDO_3(CO)_{10}$ (**2**); its T_1 is definitely long than that found for $H_2Os_3(CO)_{10}$ (**1**), and their difference allows an accurate evaluation of the dipole–dipole relaxation rate between the two equivalent hydrides[4]

$$R^{DD} = \frac{1}{T_1^{DD}} = \left\{\frac{1}{T(1)} - \frac{1}{T(2)}\right\} \cdot \frac{1}{0.96} \ [s^{-1}]$$

Now, applying the usual equation[5] for $1/T_1^{DD}$ for the intramolecular ^1H–^1H interaction in the fast correlation time limit, we get

$$r_{H\text{-}H} = \sqrt[6]{\frac{3}{2}\gamma_H^4 \hbar^2 \tau_c T_1^{DD}}$$

and using a τ_c value of 25 ps (which proved to be satisfactory in the study of ^{13}C and ^{17}O relaxation behavior in the same molecule[6]), we have calculated a r_{H-H} distance of 2.35 ± 0.03 Å. This distance is very similar to that found in the solid state from a neutron diffraction study (2.37 Å).[7]

An analogous approach could be used to calculate the M–H distance if different metal isotopes are available. This is the case of the $[Pt(PEt_3)_3H]BF_4$ complex reported in ref 2, for which the hydride-T_1 measurement for the ^{195}Pt isotopomer ($I = {}^1/_2$) is slightly shorter (2.03 s) than the corresponding T_1 in the isotopomer having $I = 0$ platinum nuclei (2.38 s). The dipolar contribution to the hydride relaxation rate due to the magnetically active ^{195}Pt is then equal to 0.0724 s^{-1}; assuming τ_c = 60 ps (reasonable value for ionic mononuclear complex), a Pt–H distance of 1.67 Å would be obtained.

Experimental Section

Compounds **1**,[8] **3**,[8] **4**,[9] **5**,[9] **6**,[9] **7**,[3] **8**,[10] and **9**[11] were obtained by literature methods; their purity was checked by the usual spectroscopic techniques, i.e. MS, IR, and ^1H NMR.

Compound **2** was obtained by reacting $Os_3(CO)_{12}$ (150 mg, 0.165 mmol) (**1**) with D_2 (4.43 mmol) in a sealed vial at + 110 °C for 12h; after TLC workup, a mixture of the fully deuterated species $D_2Os_3(CO)_{10}$[12,13] and the monodeuteriated derivatives $HDOs_3(CO)_{10}$ (**2**) was achieved in a 9:1 molecular ratio. Since ^1H NMR cannot discriminate between **1** and **2**, the identity of **2** was verified from the observation of the isotopic shift of the two equivalent CO groups trans to the metal–metal bonds on the osmium atoms bridged by the hydrido ligands. These resonances fall at 176.085, 175.925, and 175.765 ppm in **1**, **2**, and $D_2Os_3(CO)_{10}$, respectively.

NMR measurements were carried out on a JEOL GX-270/89 spectrometer. The samples were prepared by using Schlenk tube techniques and oxygen-free $CDCl_3$. The nonselective inversion–recovery pulse sequence was used to obtain T_1 values. Errors are estimated to be ±5%.

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Registry No. $H_2Os_3(CO)_{10}$, 41766-80-7; $HDOs_3(CO)_{10}$, 81293-87-0; $H_2Os_3(CO)_{11}$, 56398-24-4; $H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{12}$; $H_4Ru_4(CO)_{11}PPh_3$, 34742-79-5; $H_4Ru_4(CO)_9[P(OEt)_3]_3$, 72950-52-8; $HRu_3(CO)_9(MeCCHCMe)$, 56943-13-6; $H_2Ru_3(CO)_9(MeC{=}CEt)$, 108189-63-5; $H_2Os_3(CO)_9(C{=}CH_2)$, 42765-74-2.

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High-Resolution Solid-State ^{13}C NMR Study of Bis(2,4-pentanedionato)zinc Complexes

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High-resolution solid-state ^{13}C NMR spectroscopy,[1] involving the combined techniques[2] of cross-polarization (CP)[3] and magic-angle spinning (MAS),[4] and X-ray powder diffraction were used to study anhydrous (monomeric) (**1**), hydrated (**2**), and trimeric (**3**) bis(2,4-pentanedionato)zinc. The results were interpreted, in combination with published structural information, to derive a correlation between the geometry of the carbonyl groups and the delocalization of the π electrons in the acetylacetonate ligands. A novel metastable phase, and its phase behavior, was also investigated.

A early crystal structure of **2** is available.[5] The zinc atom is coordinated by a distorted tetragonal ZnO_5 pyramid, and the intramolecular local configurations around the four carbonyl groups in **2** are identical within ±2° in angle and ±0.04 Å in bond length. We therefore expect the π electrons to be localized. Only

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