solvent), each electrophile cleanly produces the same molybdenum complex, being the product of formal abstraction of two H^- units from MoH_4P_4. In this superficial sense, the silver reaction resembles chloride abstraction using Ag^+, with the difference being the relative stability of AgCl and AgH.

Our future work will explore the limits of weakly coordinating solvents, S, which will still permit eq 9 and 10.

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Registry No. 1, 83096-28-0; $MoH_4(PMe_2Ph)_4$, 40209-71-0; $[MoH_2(PMe_2Ph)_3(CH_3CN)_3](BF_4)_2$, 83096-30-4; $MoH_4(PMePh_2)_4$, 32109-07-2; $[MoH_2(PMePh_2)_3(CH_3CN)_3](BF_4)_2$, 83096-32-6; $MoCl_3(THF)_3$, 31355-55-2; $HBF_4{\cdot}Et_2O$, 67969-82-8; $AgBF_4$, 14104-20-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratorium für Anorganische Chemie,
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Some Cationic Bis(hydrido)-Bridged Platinum–Iridium Complexes

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The preparation of some bimetallic hydrido-bridged cationic species of the type $[L'RPt(\mu\text{-}H)_2IrHL_2L']^+$ (for L = L′ = PEt_3, R = H (3) and Ph (4); for L = PEt_3 and L′ = $P(i\text{-}Pr)_3$, R = H (5)), from *trans*-$[PtR(MeOH)L_2]^+$ and $[IrH_5L_2]$ is described. The reaction of 3 with CO gives $[IrH_2(CO)(PEt_3)_3]^+$ and some Pt/CO/PEt_3 clusters, with C_2H_4 gives $[(PEt_3)(Et)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$ (**6**), and with H_2 gives $[(PEt_3)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+$ (**8**). The reaction of **6** and H_2 gives C_2H_6 and **8**. The ^1H, ^{31}P, and some ^{13}C NMR data are reported and used for structural assignment.

Introduction

While mono(hydrido) complexes of platinum(II) have been known for a considerable time,[2,3] the isolation of bis(hydrido) complexes of the types *trans*-$[PtH_2L_2]$ (L = tertiary phosphine)[4-7] and *cis*-$[PtH_2(LL)]$ (LL = chelating di(tertiary phosphine) having bulky substituents on the phosphorus atom)[8,9] has been reported more recently. Several types of hydrido-bridged binuclear platinum complexes have also been described during the last three years.[10-17] We report here the preparation, spectroscopic characterization, and some reactivity studies of a class of bimetallic platinum–iridium complexes containing double hydrido bridges. A preliminary account of some of this work has appeared elsewhere.[18]

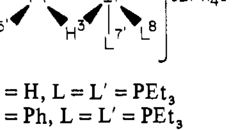
Results and Discussion

Preparative Studies. The hydrido-bridged bimetallic platinum–iridium complexes **3–5** were prepared according to eq 1. This synthetic route is an extension of a general reaction

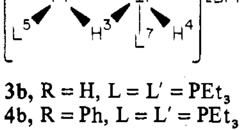
$$trans\text{-}[PtR(MeOH)L_2]^+ + [IrH_5L'_2] \rightarrow \mathbf{3\text{–}5} + H_2 + MeOH \quad (1)$$

1a, R = H, L = PEt_3
b, R = H, L = $P(i\text{-}Pr)_3$
c, R = Ph, L = PEt_3

2a, L′ = PEt_3
b, L′ = $P(i\text{-}Pr)_3$



3a, R = H, L = L′ = PEt_3
4a, R = Ph, L = L′ = PEt_3
5a, R = H, L = PEt_3; L′ = $P(i\text{-}Pr)_3$
6a, R = C_2H_5, L = L′ = Et_3P



3b, R = H, L = L′ = PEt_3
4b, R = Ph, L = L′ = PEt_3
6b, R = C_2H_5, L = L′ = PEt_3

that has been used in this laboratory to prepare binuclear hydrido-bridged complexes: labile, coordinated solvent molecules can easily be displaced, not only by two-electron donors[19] but also by hydrido complexes, giving bimetallic hydrido-

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(1) On leave of absence from Istituto di Chimica delle Macromolecole, Consiglio Nazionale delle Ricerche, Milan, Italy.

(2) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers, London, 1973.

(3) U. Belluco, "Organometallic and Coordination Chemistry of Platinum", Academic Press, New York, 1974.

(4) B. L. Shaw and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 918 (1974).

(5) A. Immirzi, A. Musco, G. Carturan, and U. Belluco, *Inorg. Chim. Acta*, **12**, L23 (1975).

(6) J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).

(7) T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).

(8) C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 365 (1975).

(9) T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, **100**, 2063 (1978).

(10) M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 801 (1978).

(11) G. Minghetti, B. Banditelli, and A. L. Bandini, *J. Organomet. Chem.*, **139**, C80 (1977).

(12) G. Minghetti, A. L. Bandini, G. Banditelli, and F. Bonati, *J. Organomet. Chem.*, **179**, C13 (1979).

(13) M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 516 (1978).

(14) G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura, and L. Zambonelli, *Angew. Chem.*, **90**, 826 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 778 (1978).

(15) G. Bracher, D. M. Grove, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem.*, **91**, 169 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 155 (1979).

(16) T. H. Tulip, T. Yamagata, T. Yoshida, R. D. Wilson, J. A. Ibers, and S. Otsuka, *Inorg. Chem.*, **18**, 2239 (1979).

(17) H. C. Clark, A. B. Goel, R. G. Goel, and W. O. Ogini, *J. Organomet. Chem.*, **157**, C16 (1978).

(18) A. Immirzi, A. Musco, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem.*, **92**, 744 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 721 (1980).

(19) H. C. Clark, C. R. Jablonski, and C. S. Wong, *Inorg. Chem.*, **14**, 1332 (1975).

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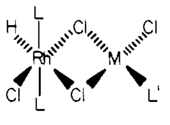
bridged species.[14,15] We now find that the hydrogen atoms in **2**, or species derived from **2**, are sufficiently nucleophilic to act as donor atoms capable of displacing the coordinated solvent molecule in **1**.

As is apparent in eq 1, the transfer of a tertiary phosphine from platinum to iridium occurs during the reaction. Transfer reactions of this type are rather uncommon although mixed tertiary phosphine complexes of the type *trans*-$[MCl_2LL']$ (M = Pd and Pt; L and L′ = tertiary phosphine) have been obtained by reaction of species such as $[RhHCl_2L_2]$ and $[M_2Cl_4L'_2]$ and binuclear intermediates of type **7** have been characterized spectroscopically.[20]



7

An important feature of these phosphine-exchange reactions appears to be the presence of at least one coordinatively unsaturated metallic center. In the case of the formation of compounds **3** and **4** it is presumed that the initially formed complex between **1** and **2** induces the loss of H_2, leaving a coordinatively unsaturated iridium(III) species of the type "IrH_3L_2", which activates the phosphine transfer.

Very extensive phosphine scrambling can occur during the reaction shown in eq 1. The reaction of **1a** with **2b** gave cation **5a**, which was isolated as its BPh_4 salt. As can be seen, during the formation of **5a** three phosphines changed metal centers. It is noteworthy that the reaction of **1b** with **2a** also gives **5a** although, in this case, the reaction formally involves the exchange of only one phosphine. This result can be interpreted by assuming either that both reactions go through a common intermediate or that the activation energy for phosphine exchange is very low and that the geometry of the final product is determined by electronic and/or steric factors.

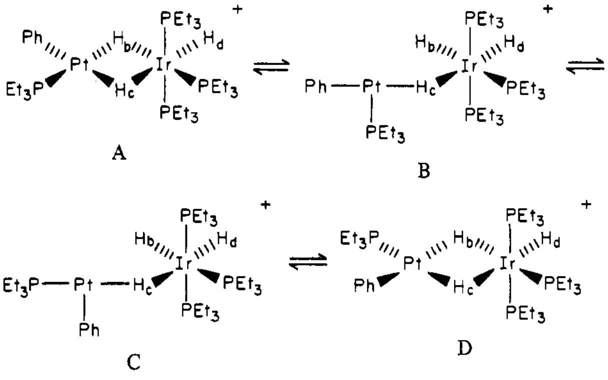
Solution Studies of Complexes 4. The isomeric pair **4a** and **4b** was detected in solution. Their structure elucidation was based on the X-ray structure determination of **4a** and on ^1H and ^{31}P NMR spectroscopic data (see Table I).

A preliminary X-ray structure determination[18] has shown that the BPh_4 salt of **4**, after recrystallization from $CH_2Cl_2/MeOH$, has structure **4a** with the equatorial phosphines on platinum and iridium in a cisoid arrangement. The ^{31}P NMR spectrum of **4a** dissolved in CD_2Cl_2, with the solution precooled to −60 °C, is fully consistent with that of the solid-state structure. When, however, this solution is allowed to warm up to room temperature or when a sample of **4a** is dissolved in CD_2Cl_2 at room temperature, the ^{31}P NMR spectrum of the solution shows the presence of equivalent amounts of **4a** and **4b**. The most striking difference between their ^{31}P NMR spectra is the value of the four-bond coupling constant between the phosphorus atom bound to platinum and the equatorial phosphorus atom bound to iridium, $^4J(P^5,P^8)$. This is 43 Hz for **4a**, in which P^5 and P^8 have a cisoid arrangement, and ca. 0 for **4b**, in which P^5 and P^8 show a transoid geometry. This difference provides a very simple criterion for the differentiation of the two isomeric forms.

Evidence for the presence of a terminal hydride ligand bound to iridium and of two bridging hydride ligands is provided by the ^1H NMR spectra (see Table I), which have been recorded both for solutions made up and measured at low temperature and for solutions containing isomeric mixtures.

The assignment of the bridged hydrogen atoms of **4a** is straightforward as only proton H^2 has two large ^2J(P,H-trans) coupling constants. The assignment of the corresponding resonances for **4b** is less unambiguous as both H^2 and H^3 have large ^2J(P,H-trans) coupling constants. The assignment proposed in Table I relies on the assumption, verified by spin-decoupling experiments, that ^2J(H,H-trans) > ^2J(H,H-cis). Further support for the proposed assignment comes from the comparison of the chemical shifts of the bridging hydrogen atoms in complex **9** (see the following discussion and Table I), which have a P–Pt–H–Ir–H arrangement analogous to that occurring in H^2 in **4b** (δ = −5.4 and −4.2, respectively).

Information about the isomerization mechanism **4a** ⇌ **4b** is provided by "spin-saturation" experiments[21] conducted at room temperature on the equilibrium mixture of these two isomers. Saturation of the resonance of the terminal hydrogen atom bound to iridium, H^4, of one isomer produces a decrease (ca. 50%) of the integrated intensity of the resonance of the corresponding hydrogen atom, H^4, in the other isomer. Additional evidence is provided by selective saturation of the signals due to the bridging hydrogen atoms H^2 and H^3. Saturation of H^3 of isomer **4a** causes an approximately 50% reduction of the integrated intensity of H^2 of isomer **4b** and vice versa. Analogously, saturation of H^2 of isomer **4a** affects the integrated intensity of H^3 of isomer **4b** and vice versa. This implies that this isomerization process occurs without exchange of terminal and bridging hydride ligands. No attempts have been made to obtain rate parameters in view of the uncertainty inherent in the results obtained.[21] These results can be rationalized on the basis of the equilibria shown in eq 2.



(2)

The initial step in the isomerization process consists in the cleavage of the Pt–H_b bond in complex A (isomer **4a**). The resulting three-coordinate platinum(II) moiety of intermediate B, as pointed out by Thorn and Hoffmann,[22] is Jahn–Teller active with preferred T- or Y-shaped C_{2v} structure. As low isomerization barriers are predicted for the interconversion of this C_{2v} unit, the T-shaped platinum fragment can be considered as a dynamic system. Thus, there would be a low activation-energy barrier for the formation of intermediate C, which could close to form product D, i.e., isomer **4b**.

Other isomerization mechanisms have also been considered, e.g., ligand-catalyzed isomerization at the platinum(II) center. However, we observe that solvents of greater donor power than those used cause irreversible chemical changes and that the addition of phosphines leads to the formation of a complex mixture of products. Thus these observations, taken in conjunction with these "spin-saturation experiments", lead us to conclude that the proposed three-coordinate intermediate is the simplest and most plausible pathway.

Solution Studies of Compound 5. The behavior of this compound is quite different from that of **4**. The ^{31}P and ^1H NMR spectra of solutions of **5**, made up at low temperature, showed only one set of signals attributable to the sole presence

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(20) R. Huis, and C. Masters, *J. Chem. Soc., Dalton Trans.*, 1796 (1976).

(21) J. W. Faller, in "Determination of Organic Structures by Physical Methods", F. C. Nachod and J. J. Zuckerman, Eds., Academic Press, New York, 1973.

(22) D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2079 (1978).

Table I. NMR Data for Complexes **3-8**[a]

compd		NMR data
3a	δ	$H^1, -20,49; H^2, -9.85; H^3, -5.48; H^4, -13.89^b$
		$P^5, 22.0; P^6, -4.3; P^8, 6.9^c$
	J	${}^1J(H^1,Pt) = 1058, {}^1J(H^2,Pt) = 670, {}^1J(H^3,Pt) = 730$
		${}^2J(H^1,P^5) = 24, {}^2J(H^2,P^5) \approx {}^2J(H^2,P^8) \approx 66, {}^2J(H^2,P^6) = 15, {}^2J(H^3,P^6) = 7, {}^2J(H^4,P^6) = {}^2J(H^4,P^8) = 15$
		${}^2J(H^1,H^2) < 3, {}^2J(H^1,H^3) \approx 6, {}^4J(H^1,H^4) \approx 9, {}^2J(H^2,H^4) < 3, {}^2J(H^3,H^4) \approx 6$
		${}^1J(Pt,P^5) = 3300, {}^3J(Pt,P^6) = 42$
		${}^2J(P^6,P^8) = 18, {}^2J(P^5,P^6) = 4, {}^4J(P^5,P^8) = 35$
3b	δ	$H^1, -23.97; H^2, -5.32; H^3 = -10.42; H^4, -13.70^b$
		$P^5, 22.3; P^6, -3.8; P^8, 5.5$
	J	${}^1J(H^1,Pt) = 1204, {}^1J(H^2,Pt) = 803, {}^1J(H^3,Pt) = 572$
		${}^2J(H^1,P^5) = 24, {}^2J(H^2,P^5) = 81, {}^2J(H^2,P^6) = 6, {}^2J(H^3,P^6) = 15$
		${}^2J(H^3,P^8) = 73, {}^2J(H^4,P^8) \approx {}^2J(H^4,P^6) \approx 18$
		${}^2J(H^1,H^2) < 3, {}^2J(H^1,H^3) \approx 6, {}^2J(H^2,H^4) \approx 6, {}^2J(H^3,H^4) < 3$
		${}^1J(Pt,P^5) = 3062, {}^2J(Pt,P^6) = 18$
		${}^4J(P^5,P^6) = 4, {}^4J(H^1,P^8) = 24, {}^4J(P^5,P^8) \approx 0$
4a	δ	$H^2, -9.04; H^3, -7.05; H^4, -15.27^d$
		$P^5, 16.3; P^6, -4.5; P^8, 6.0^e$
	J	${}^1J(H^2,Pt) = 662, {}^1J(H^3,Pt) = 671$
		${}^2J(H^2,P^5) \approx 68, {}^2J(H^2,P^6) = 15, {}^2J(H^2,P^8) \approx 68, {}^2J(H^3,P^5) = {}^2J(H^3,P^6) = {}^2J(H^3,P^8) = 6$
		${}^2J(H^4,P^8) \approx 18, {}^2J(H^4,P^6) = 15$
		${}^2J(H^2,H^4) < 3, {}^2J(H^3,H^4) = 6$
		${}^1J(Pt,P^5) = 3656, {}^3J(Pt,P^6) = 40$
		${}^2J(P^6,P^8) = 18, {}^4J(P^5,P^8) = 43, {}^4J(P^5,P^6) = 4$
4b	δ	$H^2, -4.18; H^3, -11.64; H^4, -14.64^d$
		$P^5, 18.7; P^6, -2.3; P^8, 5.6^f$
	J	${}^1J(H^2,Pt) = 826, {}^1J(H^3,Pt) = 525$
		${}^2J(H^2,P^5) = 85, {}^2J(H^2,P^6) \approx 6, {}^2J(H^2,P^8) \approx 8, {}^2J(H^3,P^5) = 6, {}^2J(H^3,P^6) = 15$
		${}^2J(H^3,P^8) = 72, {}^4J(H^4,P^5) = 24, {}^2J(H^4,P^6) = 15, {}^2J(H^4,P^8) = 15, {}^2J(H^2,H^4) \approx 6, {}^2J(H^3,H^4) < 3.$
		${}^1J(Pt,P^5) = 3349, {}^3J(Pt,P^6) = 36, {}^2J(P^5,P^6) = 4, {}^2J(P^6,P^8) = 18$
5a	δ	$H^1, -21.95,^c H^2, -10.75;^e H^3, -6.00;^e H^4, -14.71^c$
		$P^5, 53.7; P^6, -9.8; P^7, 34.2; P^8, 0.1^g$
	J	${}^1J(H^1,Pt) = 1025, {}^1J(H^2,Pt) = 670, {}^1J(H^3,Pt) = 875, {}^2J(H^1,P^5) = 23, {}^2J(H^2,P^5) \approx {}^2J(H^2,P^8) \approx 63$
		${}^2J(H^2,P^6) \approx {}^2J(H^2,P^7) \approx 15, {}^2J(H^1,H^2) < 3, {}^2J(H^1,H^3) \approx 6, {}^2J(H^1,H^4) = 9$
		${}^1J(Pt,P^5) = 3425, {}^3J(Pt,P^6) = 59, {}^3J(Pt,P^7) = 19, {}^3J(Pt,P^8) = 105$
		${}^4J(P^5,P^8) = 32, {}^2J(P^6,P^7) = 292, {}^2J(P^7,P^8) = 15, {}^4J(P^5,P^6) = 4$
		${}^2J(P^6,P^8) = 18, {}^4J(P^5,P^7) = 4$
6a	δ	$H^2, -9.78; H^3, -6.67; H^4, -14.15^g$
		$P^5, \sim 21.4; P^6, -7.7; P^8, \sim 2.9$
	J	${}^1J(H^2,Pt) \approx 645, {}^1J(H^3,Pt) \approx 650$
		${}^2J(H^2,P^5) \approx {}^2J(H^2,P^8) \approx 68, {}^2J(H^2,P^6) = 15, {}^2J(H^3,P^6) \approx 6$
		${}^2J(H^4,P^6) = 15, {}^2J(H^4,P^8) = 18, {}^2J(H^3,H^4) \approx 6$
		${}^4J(P^5,P^8) = 42, {}^4J(P^5,P^6) = 4, {}^2J(P^6,P^8) = 19$
6b	δ	$H^2, -5.05; H^3, -11.5; H^4, -14.6^g$
		$P^5, 22.8; P^6, -5.2; P^8, 2.4$
		$CH_2(Et), 4.32; CH_3(Et), 23.04$
		$CH_2(P^5), 17.59; CH_2(P^6), 26.01; CH_2(P^8), 21.87$
		$CH_3(P^5), CH_3(P^8), 8.44; CH_3(P^6), 9.33$
	J	${}^1J(H^2,Pt) = 823, {}^1J(H^3,Pt) = 512$
		${}^2J(H^2,P^5) = 83, {}^2J(H^2,P^6) = 6, {}^2J(H^2,P^8) = 8, {}^2J(H^3,P^5) \approx 5, {}^2J(H^3,P^6) = 15$
		${}^2J(H^3,P^8) = 76, {}^2J(H^4,P^5) \approx 25, {}^2J(H^4,P^6) = {}^2J(H^4,P^8) = 17, {}^2J(H^2,H^4) \approx 6, {}^2J(H^3,H^4) < 3$
		${}^1J(P^5,Pt) = 3614, {}^3J(P^6,Pt) = 59, {}^3J(P^8,Pt) = 60$
		${}^4J(P^5,P^6) = 3, {}^2J(P^6,P^8) = 17$
		${}^1J(CH_2(Et),Pt) = 572, {}^2J(CH_3(Et),Pt) \approx 31$
		${}^1J(CH_2,CH_3(Et)) = 33, {}^2J(CH_2(Et),P^5) = 8, {}^4J(CH_2(Et),P^8) = 9$
		${}^2J(CH_2\,(P^5),Pt) \approx 44; {}^1J(CH_2,P^5) = 36, {}^1J(CH_2,P^6) + {}^3J(CH_2,P^7) = 34$
		${}^1J(CH_2,P^8) = 32$
8	δ	$H^1, -11.33; H^2, -12.73^g$
		$P^1, -9.6; P^2, -21.3$
	J	${}^2J(H^1,H^2) = 4, {}^2J(H^1,P^1) = 17, {}^2J(H^1,P^2) = 17$
		${}^2J(H^2,P^1) = 18, {}^2J(H^2,P^2) = 109, {}^2J(P^1,P^2) = 16$
9	δ	$H^2, -5.37; H^4, -22.41^g$
		$P^1, 21.5; P^3, 20.9$
	J	${}^1J(H^2,Pt) = 786$
		${}^2J(H^2,P^{1\prime}) = 99, {}^2J(H^2,P^1) = -6, {}^2J(H^2,P^3) = -6$
		${}^2J(H^4,P^3) = -15, {}^2J(H^2,H^{4\prime}) = 6, {}^2J(H^2,H^4) < 3$
		${}^3J(H^4,Pt) = 76, {}^4J(H^4,P^1) = 26, {}^1J(Pt,P^1) = 2601$

[a] All J values are given in hertz. ^1H and ^{13}C chemical shifts are relative to Me_4Si and those of ^{31}P are relative to external H_3PO_4. A negative sign indicates a resonance to high field of the reference. [b] Acetone-d_6, −15 °C. [c] Acetone-d_6, −45 °C. [d] CD_2Cl_2, 25 °C. [e] CD_2Cl_2, −60 °C. [f] CD_2Cl_2, −30 °C. [g] Acetone-d_6, 25 °C.

of isomer **5a** (see Table I) and was temperature invariant; i.e., it did not isomerize in solution. Also in this case the structural assignment was made on the basis of the value of ${}^4J(P^5,P^8)$, which is 32 Hz. It is presumed that this isomeric form also occurs in the solid state.

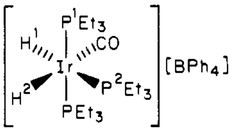
The ^1H NMR spectrum of **5a** in acetone-d_6, measured at room temperature, shows broad signals for H^1 and H^3 which sharpen when the solution is cooled. Spin-saturation experiments show that also this molecule is not rigid in solution. Irradiation of the signal assigned to H^1 causes a strong decrease in the integrated intensity of H^3 and vice versa, indicating that these two hydrogen atoms undergo an exchange process. This could be of the same type as that shown in eq 2. The absence of detectable amounts of isomer **5b** does not exclude the presence of an equilibrium of the type shown in eq 2 if one assumes that at equilibrium **5a** predominates over **5b**.

Although it is not apparent why in this compound isomer **5a** should be predominant, we note that the isomeric ratio is very sensitive to the nature of R^1 and L′ (vide infra).

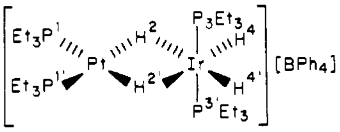
Solution Studies of Complexes 3. Solutions of species **3** exhibit a different behavior from those of **4** and **5**: the ^1H and ^{31}P NMR spectra of CD_2Cl_2 solutions, prepared and measured at −50 °C, show the presence of a 1:2 ratio of isomers **3a** and **3b** (see Table I). The set of signals observed in the ^{31}P NMR spectrum of this mixture readily allows differentiation between the two isomers. The structural assignment was done by analogy with the data obtained for complexes **4**, i.e., that $^4J(P^5,P^8)$ for the cisoid geometry as present in **3a** is large and for the transoid geometry exhibited by **3b** is small. The **3a**:**3b** isomer ratio is temperature independent. It has not been possible to establish whether (i) both isomeric forms **3a** and **3b** are already present in the solid samples of **3** or (ii) only one form is present in the solid state and isomerization occurs rapidly even at −50 °C.

The assignment of the bridged hydride ligands in **3a** and **3b** was done as described for **4a** and **4b**. The ^1H NMR signals of the hydrogen atom bound to platinum, H^1, in complexes **3a** and **3b**, which are well separated from those of the other hydride ligands, are rather broad at room temperature, suggesting that an exchange process involving these hydrogen atoms occurs on the NMR time scale. The occurrence of an exchange process has been confirmed by "spin-saturation" experiments. Irradiation of the signal due to the hydrogen atom bonded to platinum, H^1, in one of the isomers causes the disappearance of the signal due to H^1 in the other isomer and perturbation of the other hydride signals. Unfortunately the signals due to H^2, H^3, and H^4 in the spectrum of the isomeric mixture of **3a** and **3b** were not suitable for "spin-saturation" experiments because of the proximity of the resonances to be saturated and those to be observed. However, also in this case it can be assumed that the isomerization process $\mathbf{3a} \rightleftharpoons \mathbf{3b}$ is occurring and it can be presumed that it is of a nature similar to that proposed for $\mathbf{4a} \rightleftharpoons \mathbf{4b}$ shown in eq 2.

Reactions of Complexes 3 with CO, C_2H_4, and H_2. The isomeric mixture of these complexes reacts with CO, at room temperature, to yield the complex cation **8** and a mixture of platinum clusters which, on the basis of its infrared spectrum, appears to contain $[Pt_5(CO)(\mu\text{-}CO)_5(PEt_3)_4]$[23] and $[Pt_4(CO)_5(PEt_3)_4]$.[24]



8



9

Cationic species of type **8** are known, e.g., $[IrH_2(CO)(PMe_2Ph)_3]^+$, which was obtained by H_2 oxidative addition of $[Ir(CO)(PMe_2Ph)_4]^+$.[25] The platinum clusters are likely to be formed by loss of H_2 from an intermediate such as $[PtH_2(CO)(PEt_3)]$, which was not isolated.

Compounds **3** react smoothly with ethene, at room temperature, to yield the ethyl derivative **6b**. The ^1H and ^{31}P NMR spectra of a solution prepared by dissolving the solid in a precooled solvent shows the presence of a single isomer. The room-temperature spectra, however, show also the presence of a minor component (ca. 1%). Also in this case the value of the $^4J(P,P)$ coupling constant was used for the assignment of geometry, and on this basis, the predominant isomer in solution, and that occurring in the crystalline material, was shown to have the transoid geometry **6b**. The minor isomer was assigned structure **6a**. The relevant NMR data for the two complexes are given in Table I. The presence of an ethyl group bound to platinum in **6b** was confirmed by ^{13}C NMR measurements done on a sample obtained by reacting **3** with $^{13}C_2H_4$ (see Table I). The values of the $J(^{195}Pt,^{13}C)$ coupling constants allow the assignments of the signals at $\delta = 4.32$ ($^1J(Pt,C) = 572$ Hz) and $\delta = 23.04$ ($^2J(Pt,C) \approx 31$ Hz) to the methylene and methyl carbon atoms, respectively. Weak resonances at $\delta = 6.95$ and 21.44 are also observed, and these are likely to arise from the ethyl group of isomer **6a**. It is noteworthy that the geometric isomer found in the solid state in the case of the ethyl derivative has the transoid geometry **6b**, while the corresponding phenyl compound occurs in the cisoid form **5a**. Similar differences are also found in solution, where the isomeric ratios are **6a**:**6b** = ca. 1:99 and **5a**:**5b** = ca. 1:1. The reason for this difference is not apparent.

Compounds **6** react with H_2 at moderate pressures and temperatures to yield ethane and cation **9**, which could be isolated from the reaction mixture in good yield as its BPh_4 salt. The structure of **9** has been elucidated by ^1H and ^{31}P NMR spectroscopy, and the relevant data are given in Table I. During the formation of this compound, transfer of one phosphine from iridium to platinum has occurred. This phosphine transfer from one metal center to another appears to be a frequently recurring feature of the chemistry of bimetallic hydrido-bridged complexes.

The mechanism of the ethane formation appears to be complex as the reaction of **6** with D_2 produces C_2H_6 and C_2H_5D in a 2:1 ratio together with small quantities of $C_2H_4D_2$. The mechanism of this reaction, as well as the catalytic properties of complexes **3**, requires further investigation. It will only be noted here that compound **9** can also be obtained by the action of H_2 on compounds **3**.

The ^1H NMR spectrum of compound **9** requires some comment. The signals due to H^2 consist of a doublet with its ^{195}Pt satellites. The resonances are broad, even at low temperature, and show a slight asymmetry. Irradiation at the frequency of H^4 produces a spectrum clearly showing the asymmetry and considerable fine structure. This spectrum is consistent with a spin system of the type $AA'B_2XX'$ ($P^1P^{1'} = AA'$, $P^3P^{3'} = B_2$, $H^2H^{2'} = XX'$). Computer simulation[26] shows that the spectrum of H^2 can only be reproduced if it is assumed that $^2J(H^2,P^{1'})$ as well as $^2J(H^2,P^3)$ must have opposite signs. By analogy with previous work on related compounds[27] we tentatively assign a positive sign to $^2J(H^2,P^{1'})$ and a negative sign to the others.

Experimental Section

The preparation of the complexes was carried out under an atmosphere of nitrogen. Solvents were degassed before use. Elemental analyses were carried out by the Microanalytical Laboratory of the Laboratorium für Organische Chemie at ETH Zurich. The sealed NMR tubes were prepared with the use of vacuum-line techniques. The ^1H NMR spectra were recorded at 90 MHz with a Bruker HX 90 or at 250 MHz with a Bruker WM 250 spectrometer. The ^{31}P NMR spectra were recorded with the same spectrometers at 36.43 and 101.2 MHz, respectively. The ^{13}C NMR spectra of compounds **6** were recorded at 62.860 MHz with a Bruker WM 250 spectrometer.

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(23) J.-P. Barbier, R. Bender, P. Braunstein, J. Fischer, and L. Ricard, *J. Chem. Res., Synop.*, 230 (1978); *J. Chem. Res., Miniprint*, 2913 (1978).

(24) F. Moor, L. M. Venanzi, and A. J. Welch, unpublished observations.

(25) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 3356 (1970).

(26) PANIC (Parameter Adjustment in NMR by Iteration Calculation), Bruker Spectrospin, 1980.

(27) B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc. D*, 846 (1970).

The sample used for this measurement was prepared as follows: $^{13}CH_2{=}^{13}CH_2$, MSD Isotope, 90% enriched (0.025 g), was introduced by standard vacuum-line techniques into a 10-mm diameter tube containing **3** (0.16 g) in acetone-d_6 (3 mL). The NMR tube was then sealed and left overnight at room temperature before recording the ^{13}C NMR spectrum. $[IrH_5(PEt_3)_2]$,[28] *trans*-$[PtHCl(PEt_3)_2]$,[29] and *trans*-$[PtCl(Ph)(PEt_3)_2]$[30] were prepared as described in the appropriate references. $[IrH_5(P(i\text{-}Pr_3))_2]$[31] was prepared by reacting $[IrH_2Cl(P(i\text{-}Pr_3))_2]$[32] with $LiAlH_4$ in tetrahydrofuran. The other compounds were prepared as described below.

***trans*-$[PtHCl(P(i\text{-}Pr_3))_2]$.** $P(i\text{-}Pr_3)$ (0.8 mL, ca. 4 mmol) was added to a suspension of $[Pt_4Cl_4(allyl)_4]$[33] (0.406 g, 0.37 mmol) in methanol (10 mL). NaOMe (10 mL of a 0.8 M solution in MeOH) was added to the resulting colorless solution, and the reaction mixture was evaporated to dryness after stirring for 2 h at room temperature. The white residue was washed with water and dried under high vacuum. Crystallization from warm methanol gave the product as a white crystalline material (0.62 g), which was identified by IR and NMR.

Compounds 3. $Ag[BF_4]$ (0.180 g, 0.92 mmol) in methanol (5 mL) was added to a stirred solution of *trans*-$[PtHCl(PEt_3)_2]$ (0.431 g, 0.92 mmol) in methanol (5 mL). The precipitate of AgCl was filtered off, and a solution of $[IrH_5(PEt_3)_2]$ (0.400 g, 0.92 mmol) in methanol (0.8 ml) was added to the filtrate. Rapid gas evolution was observed, and a yellow solution was obtained. $Na[BPh_4]$ (0.316 g, 0.92 mmol) in methanol (7 mL) was gradually added, and the product separated out as a yellow microcrystalline solid. The mixture was stirred for 15 min, and the solid was filtered off while the mother liquor was stored at −20 °C. The solid was washed with methanol, water, and methanol successively and then dried in vacuo (0.730 g). The mother liquor, kept at −20 °C, gave a second crop of product (0.133 g); overall yield ca. 79%. Compounds **3** can be recrystallized from dichloromethane/methanol. Anal. Calcd for $BC_{48}H_{84}IrP_4Pt$: C, 48.73; H, 7.10; P, 10.49. Found: C, 48.86; H, 7.30; P, 10.21.

Compound 4a. $Ag[BF_4]$ (0.143 g, 0.73 mmol) in methanol (0.3 mL) was added to a suspension of *trans*-$[PtCl(Ph)(PEt_3)_2]$ in methanol. AgCl was filtered off, and $[IrH_5(PEt_3)_2]$ (0.319 g, 0.73 mmol) in methanol (5 mL) was added to the colorless filtrate. The resulting solution was treated with a solution of $Na[BPh_4]$ (0.252 g, 0.73 mmol) in methanol (5 mL). The product precipitated as a yellow microcrystalline solid, which was filtered off (0.663 g, 72%). This was recrystallized from CH_2Cl_2/MeOH. Anal. Calcd for $BC_{54}H_{88}IrP_4Pt$: C, 51.50; H, 7.04; P, 9.83. Found: C, 51.96; H 7.20; P, 9.94.

Compound 5a. $Ag[BF_4]$ (0.125 g, 0.64 mmol) in methanol (2 mL) was added to a solution of *trans*-$[PtHCl(PEt_3)_2]$ (0.300 g, 0.64 mmol) in methanol (10 mL). AgCl was filtered off, and the filtrate was added to $[IrH_5(P(i\text{-}Pr_3))_2]$ (0.331 g, 0.64 mmol). The resulting clear yellow solution was stirred for 1 h, and then a solution of $Na[BPh_4]$ (0.220 g, 0.64 mmol) in methanol (3 mL) was added. The product separated out as a yellow microcrystalline material (0.50 g, 61% yield). It may be recrystallized from CH_2Cl_2/MeOH. Anal. Calcd for $BC_{54}H_{96}IrP_4Pt$: C, 51.17; H, 7.63; P, 9.77. Found: C, 51.35; H, 7.75; P, 9.28.

Compound **5a** can also be prepared, in comparable yields, as described above, from *trans*-$[PtHCl(P(i\text{-}Pr_3))_2]$[34] and $[IrH_5(PEt_3)_2]$.

Compounds 6a and 6b. Ethene was bubbled, at room temperature, for 60 min through an acetone solution (25 mL) of compound **3** (0.61 g, 0.51 mmol). The resultant yellow-orange solution was reduced to ca. 5 mL and cooled to −20 °C. The product separated out as yellow prismatic crystals, which were washed with cold acetone (−80 °C) and dried under high vacuum (0.40 g, 65% yield). Anal. Calcd for $BC_{50}H_{88}IrP_4Pt$: C, 49.58; H, 7.32; P, 10.22. Found: C, 49.32; H, 7.22; P, 9.57.

Reaction of Compound 3 with CO. CO was bubbled for 30 min through a methanol solution of compound **3**, prepared from *trans*-$[PtHCl(PEt_3)_2]$ (0.173 g, 0.37 mmol) and $[IrH_5(PEt_3)_2]$ (0.160 g, 0.37 mmol). $Na[BPh_4]$ (0.127 g, 0.37 mmol) in methanol (3 mL) was added to the red solution thus obtained. The white microcrystalline precipitate thus obtained was filtered off (0.150 g, 45% yield) and proved to be compound **8**. Anal. Calcd for $BC_{43}H_{67}OP_3Ir$: C, 57.64; H, 7.53; P, 10.37. Found: C, 57.67; H, 7.53; P, 10.16. IR (Nujol, cm^{-1}): 2120–2080 (ν(IR–H)); 1980 ($\nu(C{\equiv}O)$).

The red mother liquor from the above reaction was evaporated to dryness and the residue extracted with hexane. The extract was evaporated, and the residue was recrystallized from methanol, yielding a small amount of red crystalline material with an IR spectrum showing the following bands (cm^{-1}) in the $\nu(C{\equiv}O)$ region: 1985 (s), 1980 (vw), 1880 (w), and 1850 (ms). These indicated the presence of $[Pt_5(CO)(\mu\text{-}CO)_5(PEt_3)_4]$[23] and $[Pt_4(CO)_5(PEt_3)_4]$.[24]

Reaction of Compounds 6 with H_2. A solution of compounds **6** (0.731 g, 0.30 mmol) in acetone (10 mL) was siphoned into a 70-mL stainless steel autoclave that had been previously evacuated. Hydrogen was then introduced into the autoclave up to 3.5 atm. The autoclave was kept at 60 °C for 20 h with magnetic stirring. After the system was cooled to room temperature, the gaseous portion was analyzed by gas chromatography using a Kieselgur column. This indicated the presence of ethane. The solution was evaporated under reduced pressure, and the residual yellow-orange oil, when it was stirred with methanol (2 mL), gave **9** as a yellow powder, which was filtered off, washed with methanol, and dried in vacuo (160 mg, 45% yield). The product may be recrystallized from acetone/methanol (1:3). Anal. Calcd for $BC_{48}H_{84}IrPtP_4$: C, 48.73; H, 7.18; P, 10.49. Found: C, 48.89; H, 7.10; P, 10.19.

Compound **9** is also obtained in comparable yields by reacting compounds **3** with H_2 as described for the reaction of compounds **6** with H_2.

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Registry No. 2a, 32490-60-1; **2b**, 53470-70-5; **3a**, 83025-65-4; **3b**, 83059-30-7; **4a**, 83025-67-6; **4b**, 83059-34-1; **5a**, 83025-69-8; **6a**, 83025-71-2; **6b**, 83059-32-9; **8**, 83025-72-3; **9**, 83025-74-5; *trans*-$[PtHCl(P(i\text{-}Pr)_3)_2]$, 59967-61-2; $Pt_4Cl_4(allyl)_4$, 32216-28-7; *trans*-$[PtHCl(PEt_3)_2]$, 16842-17-4; *trans*-$[PtCl(Ph)(PEt_3)_2]$, 13938-93-7; CO, 630-08-0; H_2, 1333-74-0; ethene, 74-85-1.

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(28) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965); B. E. Mann, C. Masters, and B. L. Shaw, *J. Inorg. Nucl. Chem.*, **33**, 2195 (1971).

(29) G. W. Parshall, *Inorg. Synth.*, **12**, 28 (1970).

(30) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 3543 (1971).

(31) M. G. Clerici, S. DiGioacchino, F. Maspero, E. Perrotti, and A. Zanobi, *J. Organomet. Chem.*, **84**, 379 (1975).

(32) S. Hietkamp, D. J. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, **152**, 374 (1978).

(33) J. Lukas, *Inorg. Synth.*, **15**, 79 (1974).

(34) P. G. Leviston and M. G. H. Wallbridge, *J. Organomet. Chem.*, **110**, 271 (1976).