distance of 2.43–2.46 Å.[11] Dahl et al. have suggested that an As–As distance of ~2.3 Å corresponds approximately to a double-bond length, and that in complexes of this type, the ligand bond order is decreased from 3 (free state as N_2 homologue) to 2 (on coordination) by the synergic combination of (1) the donation of electron density from the filled π orbitals of As_2 to the metal orbitals and (2) back-bonding involving the transfer of electron density from the metal orbitals into empty π^* orbitals of As_2.[5]

The two new compounds, **1** and **2**, provide a confirmation of Dahl's bonding description. Since the moieties $Co(CO)_3$ and $CpM(CO)_2$ (M = Mo or W) are isoelectronic, differences in the basicities of these groups should be reflected in the As–As bond distances. In fact, a comparison of $Co(CO)_4$ and $CpM(CO)_3$ (M = Mo or W) suggests that $Co(CO)_3$ should be a much poorer base[12] and, therefore, contribute less electron density to the As_2 π^* orbital, in keeping with Dahl's expectations.

The metal–metal bond distances ⟨average⟩ (Mo–Mo) = 3.039 (2) Å and ⟨average⟩ (W–W) = 3.020 (2) Å are within the range expected for single bonds between these elements.[13] Other bond distances and angles in **1** and **2** when compared to $Co_2(CO)_5[P(C_6H_5)_3]As_2$ agree with expectations based upon longer metal–metal bonds in **1** and **2**. Thus, the As–M–As′ angles are predictably smaller in **1** and **2**: ⟨average⟩ = 52.3 (1) and ⟨average⟩ = 52.6 (1)°, respectively, vs. 57.4 (1)° in the Co compound.

Of the known structures of complexes containing multiple As–As bonds, those involving 15-electron metal groups, i.e., $Co(CO)_3$,[5] $CpMo(CO)_2$, and $CpW(CO)_2$, bond two metal groups, form metal–metal bonds, and utilize the As_2 ligand as a four-electron donor. In contrast, the one example of a 16-electron metal group, $W(CO)_5$,[6] bonds three metal groups, does not form metal–metal bonds, and utilizes the As_2 ligand as a six-electron donor.

Recently new interest[14] in reactions of the isoelectronic cobalt carbonyl analogues of **1** and **2** has been stimulated, in part, by the observation that isolobal replacements of each of the four tetrahedral apical groups is possible. Thus, Dahl et al. have shown[5] that all members of the series $E_n[Co(CO)_3]_m$ ($n + m = 4$) can be prepared, and Seyferth et al. have shown that μ_3-alkylidyne groups also may replace either unit.[14] The possibility for substitutional replacements either for the $CpM(CO)_2$ group or the As atoms in **1** or **2** will become a subject for future study.

Acknowledgment. This work was support, in part, by a grant from the National Science Foundation.

Registry No. 1, 83025-09-6; 2, 83025-08-5; $[CpMo(CO)_3]_2$, 12091-64-4; $CpW(CO)_3H$, 12128-26-6; $(AsC_6H_5)_6$, 20738-31-2.

Supplementary Material Available: Tables of final fractionsl atomic coordinates, bond distances and angles, and structure factors (34 pages). Ordering information is given on any current masthead page.

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cis-Hydridoacylrhodium(III) Complexes Not Stabilized by Chelation. Reductive Elimination and Decarbonylation[†]

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Summary: Stable *cis*-hydridoacylrhodium complexes, *cis*-$HRh(COR)(PMe_3)_3Cl$ (R = Me, Ph, 4-C_6H_4F, OMe), are obtained by oxidative addition of RCHO to RhCl $(PMe_3)_3$ (**1**). Upon heating, these complexes undergo competing intramolecular reductive elimination of the aldehyde and decarbonylation to the alkane; the former process prevails if RCHO is removed as formed. Both these processes proceed from a common unsaturated intermediate, formation of which is probably rate determining.

Although hydridoacylmetal complexes have been postulated as intermediates in a number of very important transformations,[1] only a few such complexes have been reported.[2,3] Of particular interest are hydridoacylrhodium complexes since rhodium compounds are useful homogeneous catalysts for hydroformylation,[4] aldehyde decarbonylation,[2,5] and aldehyde hydroacylation of olefins,[2,6,7] all of which are thought to involve these complexes as intermediates. The only hydridoacylrhodium complex reported is a chelation-stabilized oxidative addition product of 8-quinolinecarboxaldehyde to RhCl $(PPh_3)_3$,[2] despite attempts to isolate such complexes.[7] We have recently found that *cis*-hydridoalkylrhodium(III) trimethylphosphine compounds are relatively stable and isolable as a result of very slow PMe_3 dissociation from them.[8] This suggests that hydridoacylrhodium trimethylphosphine complexes may be stabilized toward migratory deinsertion as well as reductive elimination, both of which probably require ligand dissociation.

Indeed, we have found that simple aldehydes undergo cis oxidative addition to $RhCl(PMe_3)_3$[9] (**1**) to afford the first stable *cis*-hydridoacylrhodium complexes not stabilized by chelation and have directly observed for the first

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[†] Contribution No. 3068.

[1] These transformations include hydroformylation, model Fischer Tropsch type syntheses, aldehyde decarbonylation, and olefin hydroacylation: J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science, Mill Valley, CA, 1980.

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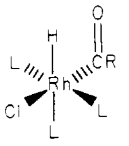
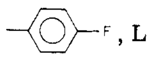
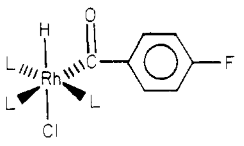
time hydridoacyl reductive elimination of a metal complex.

Addition of excess of acetaldehyde to an orange solution of **1** in toluene at 25 °C under N_2 resulted in decoloration after 10 min. Removal of the solvent under high vacuum and crystallization of the residue from toluene/pentane afforded complex **2a** in 85% yield as white crystals: IR (Nujol) 1615 (s, $\nu_{C=O}$), 1923 (s, ν_{Rh-H}); ^1H NMR (C_6D_6) δ 1.24 (d, J = 7.0 Hz, 9 H, PMe_3), 1.32 (t, J = 3.2 Hz, 18 H, 2 PMe_3), 2.35 (s, 3 H, CH_3CO), −8.26 (d of d of t, $J_{H-P,trans}$ = 190.1 Hz, $J_{H-P,cis}$ = 15.1 Hz, J_{H-Rh} = 18.1 Hz, 1 H, Rh–H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.36 (d of d, J_{P-Rh} = 114.5 Hz, J_{P-P} = 30.8 Hz, 2 P), −24.07 (d of t, J_{P-Rh} = 93.3 Hz, J_{P-P} = 30.8 Hz). Since the ^1H NMR and ^{31}P NMR spectra are consistent only with a structure containing a PMe_3 ligand trans to the hydride ligand and having two identical trans PMe_3 ligands, the hydrido and acyl ligands have to be in mutually cis positions, as shown in structure **2a**.



2a, R = CH_3, L = PMe_3
b, R = Ph, L = PMe_3
c, R = , L = PMe_3
d, R = OMe, L = PMe_3



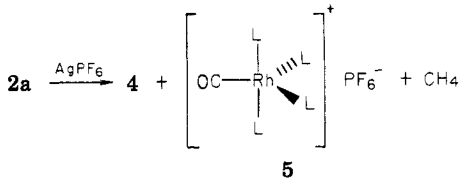
3

Oxidative addition of acetaldehyde to $[Rh(PMe_3)_4]^+Cl^-$[9] leads to the same product, although at a slower rate. $ClRh(CO)(PMe_3)_2$[9] is completely unreactive under these conditions.

A *cis*-hydridobenzoyl complex **2b**[10] is obtained similarly from **1** and benzaldehyde in 71% yield. Oxidative addition of *p*-fluorobenzaldehyde to **1** leads to the two *mer* isomers, **2c**[10] and **3**,[10] in 83% and 5% yields, respectively. Methyl formate smoothly adds to **1** to give the *cis*-hydridocarbomethoxy complex **2d**[10] in 95% yield. Complexes **2a–d** and **3** are stable at room temperature and fairly insensitive to air in the solid state. When a benzene solution of **2a–c** is heated at above 60 °C, these complexes undergo migratory deinsertion followed by reductive elimination to yield $ClRh(CO)(PMe_3)_2$ (**4**) and RH, thus resulting in overall aldehyde decarbonylation. However, reductive elimination of the aldehyde from **2** is also observed (eq 1).

$$RCHO + \underset{\mathbf{1}}{RhCl(PMe_3)_3} \rightleftarrows \mathbf{2} \rightarrow \underset{\mathbf{4}}{Rh(CO)(PMe_3)_2Cl} + RH + PMe_3 \quad (1)$$

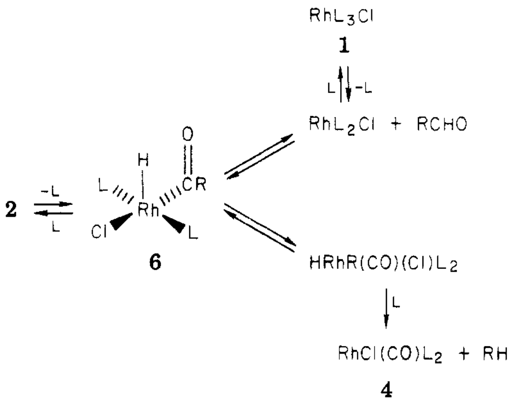
For example, heating a 0.1 M C_6D_6 solution of **2a** at 70 °C for 2 h yields methane (51% yield), acetaldehyde (14%), PMe_3 (50%), **4** (54%), **1** (15%), and recovered **2a** (31%). The observed decarbonylation process is accelerated considerably by abstraction of the chloride ligand: addition of $AgPF_6$ to a solution of **2a** in acetone at 25 °C immediately results in methane evolution, formation of **4**, and the novel complex **5**[10,11] (eq 2). However, hydridoacyl reductive elimination is the major process observed when the product aldehyde is efficiently removed: upon heating **2a** at 90 °C for 2 h while the volatile products were collected under high vacuum, complete decomposition takes place and CH_3CHO (87% yield), CH_4 (13%), and PMe_3 (19%) are formed. ^{31}P NMR of the residue shows formation of **1** (80%) and **4** (13%). This is the first reported direct observation of an hydridoacyl reductive elimination from a metal complex, a process which has been postulated as the product-forming step in olefin hydroformylation.[4] This process is *intramolecular*: complete decomposition of an equimolar mixture of *cis*-$HRh(COCH_3)(PMe_3)_3Cl$ and *cis*-$DRh(COCD_3)(PMe_3)_3Cl$[10] (obtained from oxidative addition of CD_3CDO to **1**) yielded predominantly CH_3CHO and CD_3CDO (CH_3CHO/CH_3CDO = 13, CD_3CDO/CD_3CHO = 10, determined by mass spectrometry).



(2)

5

Scheme I



L = PMe_3

We believe that reductive elimination of the aldehyde proceeds by a prior rate-determining phosphine dissociation step, as observed in the hydridoalkyl reductive elimination from rhodium(III) trimethylphoshine complexes.[8] Supporting evidence includes considerable acceleration of this process by a "phoshine sponge": addition of an equivalent amount of $(C_2H_4)_2Rh(acac)$ to a benzene solution of **2a** at 25 °C and immediate vacuum transfer of the volatile products reveals formation of acetaldehyde (54% yield) and methane (24%), in addition to the substitution product ethylene (35%) and methyl ethyl ketone (22%), the latter probably resulting from ethylene coordination to the unsaturated intermediate followed by insertion and reductive elimination (hydroacylation). Also, addition of PMe_3 to a solution of **2a** resulted in retardation of both the reductive elimination and decarbonylation processes without significantly affecting their relative rates. The phosphine trans to the hydride is the one expected to dissociate more readily because of the large hydride trans effect.[12] As a result, complex **3** is expected to be more stable than **2c**. Indeed, no decomposition of **3** takes place under conditions in which **2c** is fully decomposed (50 °C, 3 h). The *cis*-hydridoacyl complexes **2** are considerably more stable than analogous *cis*-hydridoalkyl complexes,[8] although hydridoacyl reductive elimination is expected to be more facile than reductive elimination of hydridoalkyl groups because of the M–COR bond being weaker than **M–R**.[13] This is consistent, however, with the expected,

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[10] This compound is fully characterized on the basis of IR, ^1H NMR and ^{31}P NMR spectra.

[11] Some silver metal was also formed.

[12] Only the phosphine trans to the hydride dissociates in *mer*-$RhH_2(PPh_3)_3Cl$: P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 3240 (1972).

[13] Acyl–alkyl reductive elimination from Pt(IV) is more facile than dialkyl reductive elimination: M. P. Brown, R. J. Puddephatt, C. E. E. Upton, and S. W. Lavington, *J. Chem. Soc., Dalton Trans.*, 1613 (1974).

more difficult phosphine dissociation from the hydridoacyl compounds.

On the basis of the above observations, we believe that both the reductive elimination and the decarbonylation reactions of the complexes **2** proceed from a common unsaturated intermediate, **6**, formation of which is rate determing (Scheme I). Because the hydridoalkyl reductive elimination step in the decarbonylation process is irreversible, whereas the hydridoacyl reductive elimination is reversible, the decarbonylation process usually predominates. However, if the equilibrium is interrupted either by removal of the product aldehyde or the product Rh(I) complex, e.g., by oxidative addition of hydrogen as in the hydroformylation process, the hydridoacyl reductive elimination prevails.

We are currently actively pursuing further clarification of these reactions as well as studying other reactions of hydridoacylrhodium complexes, notably, hydroacylation.

Acknowledgment. I am grateful to Dr. S. S. Wreford for helpful discussions and to Mr. M. A. Cushing, Jr., for excellent technical assistance.

Registry No. 1, 36103-64-7; **2a**, 82555-25-7; **2b**, 82978-78-7; **2c**, 82963-16-4; **2d**, 82963-17-5; **3**, 83023-45-4; **4**, 36713-95-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; $(C_6H_5F)CHO$, 459-57-4; (MeO)CHO, 107-31-3; $[Rh(PMe_3)_4]Cl$, 70525-09-6.

Structure of $(C_5H_4CH_3)_2V_2S_5$ and Its Acetylene Addition Reaction

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Summary: Thermal rearrangement of $(C_5H_4CH_3)_2VS_5$ gives high yields of $(C_5H_4CH_3)_2V_2S_5$ (**1**) whose structure consists of equivalent $(C_5H_4CH_3)V$ units bridged by μ-S, μ-η^1-S_2, and μ-η^2-S_2 ligands.

It has previously been reported that $(C_5H_5)_2VS_5$ rearranges in refluxing benzene solutions to give a poorly soluble product analyzing as $[(C_5H_5)_2V_2S_5]_n$.[1] While the precursor complex has been structurally characterized as a pentasulfido chelate,[1,2] the nature of the bimetallic product, which can also be prepared by treatment of $(C_5H_5)V(CO)_4$ with sulfur,[3] remains a mystery. This problem attracted our attention because of its relevance to the coupling reactions we recently observed in our studies on the desulfurization of $(C_5H_4R)_2TiS_5$.[4,5] X-ray diffraction quality crystals of $[(C_5H_5)_2V_2S_5]_n$ have eluded us and others;[1] however, suitable single crystals of $[(C_5H_4CH_3)_2V_2S_5]_n$ (**1**) were easily grown from dichloromethane–methanol solutions.

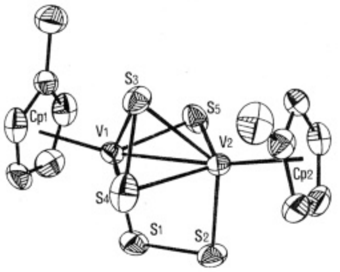

Figure 1. An ORTEP view of the $(C_5H_4CH_3)_2V_2S_5$ molecule showing the labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

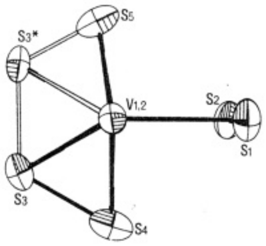

Figure 2. A view of the V_2S_5 core in $(C_5H_4CH_3)_2V_2S_5$ looking directly along the V1–V2 vector. In 19% of the molecules, S3* is present and S3 is absent. Thus, in the minority case, the S3*, S5 pair is the μ-η^2-S_2 ligand and S4 is a μ-S ligand.

Table I. Selected Bond Distances (Å) and Angles (Deg) for $(C_5H_4CH_3)_2V_2S_5$ (1)

(a) Bond Distances

V1–V2	2.658 (1)	V1–S5	2.267 (1)
V1–S1	2.316 (1)	V2–S5	2.263 (1)
V2–S2	2.315 (1)	V1–S3*	2.440 (6)
V1–S3	2.391 (2)	V2–S3*	2.414 (5)
V2–S3	2.401 (1)	S1–S2	2.023 (2)
V1–S4	2.348 (1)	S3–S4	1.956 (2)
V2–S4	2.353 (2)		

(b) Bond Angles

V1–S3–V2	67.4 (0)	V2–S4–S3	67.0 (1)
V1–S4–V2	68.9 (0)	S1–V1–V2	82.1 (0)
V1–S5–V2	71.9 (0)	S2–V2–V1	82.2 (0)
V1–S3*–V2	66.4 (1)	S3–V1–V2	56.5 (0)
V1–S1–S2	97.9 (1)	S3–V2–V1	56.1 (0)
V2–S2–S1	97.8 (1)	S4–V1–V2	55.7 (0)
V1–S3–S4	64.5 (1)	S4–V2–V1	55.5 (0)
V1–S4–S3	66.8 (1)	S5–V1–V2	54.0 (0)
V2–S3–S4	64.4 (1)	S5–V2–V1	54.1 (0)

$[(C_5H_4CH_3)_2V_2S_5]_n$ is easily prepared via the thermal rearrangement of $(C_5H_4CH_3)_2VS_5$ in refluxing toluene (7 mL/mmol of $(C_5H_4CH_3)_2VS_5$) (eq 1). After 3 h, the hot

$$(C_5H_4CH_3)_2VS_5 \xrightarrow[PhCH_3]{110\ °C} (C_5H_4CH_3)_2V_2S_5 \qquad (1)$$

toluene solution was filtered, concentrated, and cooled to −25 °C, giving analytically pure black crystals of 1 in 85% yield.[6]

The structure[7] of 1 is depicted in Figure 1, and a view of the V_2S_5 core is shown in Figure 2; important bond

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(1) Muller, K. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.

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(6) Anal. Calcd for $C_{12}H_{14}S_5V_2$ (1): C, 34.28; H, 3.36; S, 38.13; V, 24.23. Found: C, 34.28; H, 3.46; S, 38.03; V, 23.89. IR (mineral oil mull): 1067 (m), 1052 (m), 1034 (m), 931 (w), 917 (w), 889 (w), 815 (s), 602 (w), 566 (m), 534 (m), 469 (w), 430 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.59 (2 H, m), 6.38 (2 H, m), 2.38 (3 H, s). EI mass spectrum (70 eV), m/e (relative intensity): 420 (37, M^+), 356 (100, $C_{12}H_{14}S_3V_2^+$).

(7) $(C_5H_4CH_3)_2V_2S_5$ (1) crystallizes in the monoclinic space group $C2/c$ with a = 12.703 (5) Å, b = 7.917 (2) Å, c = 31.30 (1) Å, β = 102.22 (4)°, V = 3075.9 $Å^3$, Z = 8, and μ = 18.13 cm^{-1} (Mo Kα, λ = 0.71073 Å). A total of 3057 reflections ($3° \leq 2\theta \leq 50°$) were collected on a Nicolet R3 diffractometer of which 2696 reflections were unique. Of these reflections, 2300 with $F_o \geq 2\sigma(F_o)$ were used in the subsequent solution and refinement. The final discrepancy factors are 4.63 and 4.22% for R_F and R_{wF}, respectively.

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