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(11) Brominated SX8 and SX12 could be prepared without difficulty in the usual manner.[9] Combustion analysis both before and after attempted lithiation,[9] however, revealed that only about 50% of the bromines on SX8 and less than 1% of those on SX12 could be replaced. Added hexamethylphosphoramide did not improve the reaction on SX12 at −10 °C in THF. Presumably *n*-BuLi has difficulty penetrating the more highly cross-linked polystyrene beads. BIO-RAD reports[10] the following molecular weight exclusion limits: SX1(14 000), SX2 (2700), SX4 (1400), SX8 (1000), SX12 (400), and SM2 (14 000).
(12) Shorter times and lower temperatures (2 h at 0 °C) give diminished but detectable amounts of anhydride in all cases.
(13) Low levels of functionalization are practical only for polymer-bound *catalytic* species where each active site can be used many times over, e.g., R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **95**, 2373 (1973); W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, *ibid.*, **97**, 2128 (1975).
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A Vanadium Carbonyl Trihydride, $H_3V(CO)_3$diars

Sir:

While noncluster second- and third-row transition metal complexes containing more than two coordinated hydride ligands are now very common, relatively few such first-row transition metal complexes have been reported.[1] The latter are H_4FeL_3 (L = PEt_2Ph and $PBuPh_2$)[2] and H_3CoL_3 (L = various phosphines).[3] We now report that the first polyhydride complex of vanadium, $H_3V(CO)_3$diars (**1**) (diars = *o*-phenylenebis(dimethylarsine)), is formed rapidly and in good yield (60–80%) by the interaction of $[Et_4N][V(CO)_4diars]$ (**2**)[4] with excess anhydrous or aqueous HX (X = Cl, Br, I) in tetrahydrofuran (THF). The same substance is also generated more slowly but in higher initial purity from **2** and an excess of *tert*-butyl chloride suspended in water.[5,6] By monitoring infrared spectra in the carbonyl stretching region of these reactions, $HV(CO)_4$diars (**3**)[4] has been shown to initially form. Excess hydrogen chloride then reacts with **3** to generate **1** and phosgene (or CO_2 in the presence of water) in approximately equal amounts.[6] Although the formation of phosgene requires the presence of chloride ion, by varying the reaction components we have determined that a strong acid is also necessary. Thus, **2** or **3** in the presence of neutral water, aqueous NaCl, or Bu_4NCl in THF do not give **1**. Also, moderately strong acids having weakly nucleophilic conjugate bases such as aqueous H_2SO_4 and $H_4PO_{H_3}PO_4$ convert **2** to **3** but do not provide **1**. On the basis of having established the requirement of HX (X = Cl, Br, or I) and formation of phosgene[7] during the generation of **1** the following pathway for the reaction is proposed:[8]

$$\mathrm{HV(CO)_4diars + HX \rightleftharpoons [H_2V(CO)_4diars^+X^-]}$$
$$\mathrm{\rightleftharpoons [HV(CO)_3diars\{C(OH)X\}}$$
$$\mathrm{\overset{HX}{\rightleftharpoons} H_2V(CO)_3diars\{C(OH)X_2\} \rightleftharpoons H_3V(CO)_3diars + COX_2}$$
$$\mathrm{(X = Cl, Br, I)}$$

Although the overall scheme is unprecedented in metal carbonyl chemistry, the individual steps are consistent with known reactivity patterns of carbonyls.[9] For example, nucleophilic attack of coordinated carbon monoxide by a variety of groups including hydroxide and water[10] are known. Protonation of metal carbonyls also enhances the susceptibility of coordinated carbonyls towards nucleophilic attack.[11] The high coordination number of vanadium in **3** may favor protonation at a carbonyl oxygen rather than the metal center. This latter process may be crucial in permitting facile halide attack resulting in the eventual elimination of phosgene.

The physical and chemical properties of **1**, the first derivative of the unknown trianion $V(CO)_3diars^{3-}$,[12] are noteworthy. Its infrared solution spectra in THF show two intense and sharp carbonyl stretching frequencies at 1840 and 1779 cm^{-1}, which are at unusually low energy for terminal carbonyls in neutral complexes.[13,14] A strongly temperature-dependent ^1H NMR signal attributable to the hydridic protons is also observed. While the signal is too broad to detect at room temperature,[15,16] a well-defined singlet of relative intensity 3 with respect to the 12 methyl-diars protons is observed at τ 8.86 in CD_2Cl_2 at −20 °C. The signal retains its sharpness down to −70 °C. Compared to most metal hydride chemical shifts, this signal occurs at relatively low field but not unprecedentedly so.[17-20] The diars methyl groups in (I) give rise to a pair of signals of equal area at τ 8.28 and 8.54 in CD_2Cl_2 which do not broaden or coalesce between 25 and −70 °C.

In contrast to other carbonyl hydrides of vanadium,[4,16,21] **1** is quite unreactive and thermally stable.[22] For example, unlike **3**, which is readily deprotonated to form $V(CO)_4diars^-$,[4] attempts to deprotonate **1** with butyllithium failed to provide any evidence for the formation of $H_{3-n}V(CO)_3diars^{n-}$ (n = 1, 2, or 3) at −78 °C. Instead, decomposition to uncharacterized species occurred. Although we have been unsuccessful thus far in observing any parallels in the chemistry of **1** and the other known group Vb trihydrides, $M(C_5H_5)_2H_3$ (M = Nb and Ta),[23] the photolysis of **1** with an unfiltered medium-pressure mercury vapor lamp in the presence of carbon monoxide provides substantial yields of **3**.[4] Evidently, a photoinduced elimination of molecular hydrogen from **1** occurs during this process, generating coordinatively unsaturated $HV(CO)_3$diars which is trapped with carbon monoxide to provide the observed product. Similar photochemical processes have been reported recently for $IrClH_2(PPh_3)_3$ and $IrH_3(PPh_3)_3$.[24]

Potentially, the reaction of other metal carbonyls and carbonyl monohydrides with hydrogen halides under similar conditions could be an important general route to transition metal di- and trihydrides. Indeed, we have shown that the treatment of $HV(CO)_4$dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) and $Nb(CO)_4DPPE^-$ (DPPE = 1,2-bis(diphenylphosphino)ethane)[25] with *tert*-butyl chloride and water provides substances which have infrared spectra very similar to that of **1**.[26] However, analogous reactions of HCl or *tert*-butyl chloride–water with related carbonyls give either decomposition, no reaction, or other products: $HV(CO)_4DPPE$[21] (decomposition to VCl_3), $W(CO)_4$diars[27] (no reaction), $Fe(CO)_3diars$[28] (protonation, no further reaction), $HRe(CO)_5$[29] (quantitative formation of $ClRe(CO)_5$). Clearly, further studies are necessary to determine the scope and limitations of this new procedure for polyhydride synthesis.

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(5) In a typical preparation a slurry containing **2** (1.35 g) in 40 ml each of oxygen-free water and *tert*-butyl chloride is stirred for 12 h at room temperature. Initially all solids dissolve in the organic layer. After 2–4 h red crystals of **1** slowly form. Finally, all unreacted *tert*-butyl chloride is removed in vacuo. Impure **1** is filtered, washed with water to remove Et_4NCl, dried, and recrystallized from methylene chloride/heptane to provide 0.64 g (65% yield) of analytically pure **1**. Anal. Calcd (found) for $C_{13}H_9As_2O_3V$: C, 36.82; H, 4.52; As, 35.33; mol wt 424. Found: C, 36.69; H, 4.57; As, 35.61; mol wt, 420 in THF.

(6) Undoubtedly, *tert*-butyl chloride slowly hydrolyzes under these conditions to give aqueous HCl which then eventually provides **1**. In support of this interpretation, we find that **2** does not react with *tert*-butyl chloride in the absence of water.

(7) Phosgene from the reaction of anhydrous HCl with **2** or **3** in THF was isolated in the form of urea. For example, anhydrous HCl was bubbled (via all-glass tubing) through a solution of 2.00 g of **1** in 50 ml of THF. The solution rapidly changed colors from red to yellow to red. With the HCl flow stopped, the solution was stirred for 1 h and then all volatiles were removed (leaving after recrystallization) (vide supra) 1.1 g (75%) of **1**) and trapped out in a flask containing 50 ml of anhydrous ammonia. After stirring the ammonia solution for 1 h at −50 °C, all volatiles were again removed, leaving a colorless mixture of ammonium chloride and urea. Neutralization of an aqueous solution of this mixture with sodium hydroxide, followed by evaporation, left NaCl and urea which were cleanly separated by treatment with absolute ethanol. Evaporation of ethanol left 0.14 g (64% yield) of substance identical with genuine urea.

(8) No direct evidence for the formation of the bracketed intermediates has been obtained; however, clearly protonation of **3** followed by halide attack of coordinated carbon monoxide are required steps in the actual process. In the presence of water the C(OH)X grouping is likely to be hydrolyzed to a carboxyl group (vide infra). Also, as suggested by a referee, a second halide attack of the hydroxyhalocarbene may precede the protonation process.

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(26) $HV(CO)_4dmpe$ provides an unstable violet-red solid (ν(CO): 1827 and 1740 cm^{-1} in THF) while $Nb(CO)_4DPPE^-$ gives a thermally stable but incompletely characterized orange-yellow solid (ν(CO): 1834 and 1759 cm^{-1} in CH_2Cl_2).

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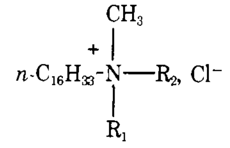
Sequential Bifunctional Micellar Catalysis

Sir:

The comparison of micelles and enzymes is now commonplace,[1] but the rational design of functionalized surfactants to provide increasingly exact enzyme analogues is a more recent venture.[2] A key feature of chymotrypsin catalysis is basic activation by an imidazole group (His-57) of the Ser-195 hydroxyl moiety; the latter's oxygen is the nucleophile which attacks the substrate's carbonyl group.[3] Many "model enzymes" have been designed to mimic this mechanism.[4] Micellar chymotrypsin models have included hydroxyl-[5] and imidazole-functionalized[6] surfactants, but few studies of *bifunctional* micellar catalysts have appeared.[7] Mechanistic exploration of these systems is crucial to the construction of useful micellar enzyme analogues.

Recently, we described the comparative effectiveness of micellized surfactants I–IV at catalyzing the cleavages of *p*-nitrophenyl acetate and hexanoate (PNPA and PNPH).[10] Based upon relative k_ψ^{max} values,[11] there seemed to be no synergism between the hydroxyl and imidazole moieties of IV and no reason to suspect significant differences in mechanistic behavior between III and IV. However, although the reaction of III with PNPA leads to the formation and decay of an acetylimidazole intermediate,[6g] readily observable at 245 nm (Figure 1, curve 1), we can observe no such intermediate during the analogous reaction of bifunctional catalyst IV (Figure 1, curve 2).[13]



$$n\text{-}C_{16}H_{33}\text{-}\overset{+}{N}(CH_3)(R_1)\text{—}R_2,\ Cl^-$$

	I	II	III	IV
R_1	CH_3	CH_3	CH_3	CH_2CH_2OH
R_2	CH_3	CH_2CH_2OH	CH_2Im^{12}	CH_2Im^{12}

From a preparative scale reaction of PNPA with IV,[14] we quantitatively isolated *O*-acetyl-IV.[15] Thus PNPA did not acetylate water under the influence of the bifunctional catalyst. The failure of IV to furnish an observable acetylimidazole intermediate in its reaction with PNPA can be explained in two ways: (a) No intermediate is visible because none is ever formed; IV behaves as a chymotrypsin analogue and undergoes direct *O*-acetylation, eq 1. (b) Alternatively, an intermediate