the three electrons added on going from vanadium to iron are populating molecular orbitals having substantial metal d_{xy} and/or $d_{x^2-y^2}$ character, one would expect an accompanying increase in the relative δ bonding and a tendency toward adoption of an eclipsed conformation. Thus, staggered conformations should be most favored for metals having low d electron configurations. In these cases ligand rotation is apparently hindered by interligand repulsions, which are induced as an eclipsed conformation is approached. For proton site exchange to occur, the eclipsed conformations must be reached.

Also very informative have been the reactions of $Ti(2,4\text{-}C_7H_{11})_2$ with Lewis bases. Thus, exposure in pentane solution to CO results in a very rapid reaction, leading to isolation of a yellow solid product. The infrared spectrum of this compound is quite indicative of a monocarbonyl adduct,[13] displaying a single sharp C–O stretching frequency at 1942 cm^{-1}. The ^1H and ^{13}C NMR spectra (Figures 3 and 4) differ markedly from those of $Ti(2,4\text{-}C_7H_{11})_2$, each displaying only four resonances attributable to the pentadienyl ligands, indicating either the restoration of the perpendicular mirror plane for the ligand or less likely a much lower activation energy to ligand rotation as compared to $Ti(2,4\text{-}C_7H_{11})_2$.[14] A reasonable structural pattern might be based upon a near cis-eclipsed ligand orientation in which the central portions of the ligands are bent toward one another so that the CO ligand is bound near the open portions of the pentadienyl ligands. A more precise understanding of the structures and energetics of these compounds, however, must await the completion of detailed variable-temperature NMR and X-ray diffraction studies.

The above results demonstrate a variety of unique properties and potential applications for pentadienyl ligands. Certainly the stabilization of a simple very electron-deficient open titanocene contrasts remarkedly with the situation observed in the corresponding cyclopentadienyl systems. Perhaps as notable is the observation that even in the presence of a strongly coordinating ligand such as CO, the observed product adopts only a 16-electron configuration. Probably by virtue of their large size and low-spin-generating properties, pentadienyl groups are quite clearly superb, and readily modifiable, ligands for the stabilization of very novel, electron-deficient complexes. Indeed, rapid reactions with PF_3 and CO_2 also take place, and the products are presently under study. These and other efforts to gain further insight into titanium–pentadienyl systems will be reported in due course.

Acknowledgment. R.D.E. expresses his gratitude for partial support of this research through grants from the University of Utah Research Committee, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. CHE-8120683). We express our appreciation to Professor Len Spicer and John Peterson for the use of their GC equipment and to Zu-Wen Qiu and Fred Morin of this department for their aid in obtaining Varian SC-300 NMR spectra.

Registry No. $(2,4\text{-}C_7H_{11})_2Ti$, 81876-06-4; $(2,4\text{-}C_7H_{11})_2Ti(CO)$, 81876-07-5.

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(12) It seems likely that the low-spin configuration of the compound also serves as a major contributing factor to compound stability. Thus, while $Fe(2,4\text{-}C_7H_{11})_2$ has Fe–C bond distances slightly exceeding those of ferrocene (both compounds being diamagnetic),[3a] the average V–C bond distance in $V(2,4\text{-}C_7H_{11})_2$[3d] (2.21 Å) is much shorter than that of $V(C_5H_5)_2$ (2.28 Å), in which three unparied electrons are present. Note that in titanocene systems, two unpaired electrons are found.[5]

(13) For comparison, the well-characterized (and more stable) $(2,4\text{-}C_7H_{11})_2V(CO)$ also has ν(CO) 1942 cm^{-1}. In $(C_5H_5)_2V(CO)$, ν(CO) is 1884 cm^{-1}. Interestingly, the titanium carbonyl is much less air sensitive (appearing unchanged in several minutes) than $(2,4\text{-}C_7H_{11})_2Ti$ but is thermally much less stable, generally decomposing in a matter of hours during either NMR or X-ray diffraction studies.

(14) For the ^1H spectrum, the resonances are observed at δ 4.73, 2.77, 1.53, and 0.82 (indirectly referenced to Me_4Si by using C_6D_5H (δ 7.23) as internal standard). In the ^{13}C spectrum, the ligand resonances appear at 116.8, 100.6, 59.3, and 29.2 ppm, with the ^{13}CO resonance at 255.9 ppm. These values are intermediate between values for the 14-electron $(2,4\text{-}C_7H_{11})_2Ti$ and 18-electron $(2,4\text{-}C_7H_{11})_2Fe$. In all cases the assignments were confirmed with the aid of proton-coupled spectra.

Evidence for Tricarbonyltrihydridocobalt(III). Synthesis from Tricarbonylhydridocobalt(I) in Matrices

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Received January 6, 1982

I recently reported that $Fe(CO)_4$ oxidatively adds H_2 to form $H_2Fe(CO)_4$ in argon matrices.[1] This was the first report of such activity for hydrogen in matrices although there were several reports of oxidative addition of methane and alkyl halides in matrices of metal atoms and clusters.[2-4] The 16-electron $HCo(CO)_3$ is of the type that is presumed to undergo oxidative addition, although there are no reports of such occurring and the product of hydrogen oxidative addition has never been reported. $HCo(CO)_3$ is formed in argon matrices by 254-nm photolysis of $HCo(CO)_4$.[5] The lifetime of this coordinatively unsaturated intermediate is short because it efficiently recombines with CO, accumulating little, even after prolonged irradiation periods. Rather than $HCo(CO)_3$, the major observed products of the photolysis of $HCo(CO)_4$ are $Co(CO)_4$ and the hydrogen atom, the products of a less efficient homolysis of the cobalt–hydrogen bond.[6] Although its lifetime is not long, $HCo(CO)_3$ does appear to react with H_2.

When argon matrices of $HCo(CO)_4$ that contain 10 mol % of H_2 are photolyzed with a low-pressure mercury lamp, changes become apparent with the same characteristic rate as CO exchange.[5] After only 5 min of photolysis several new absorptions appear in the carbonyl region of the infrared spectrum. To show that the changes are not due to an impurity, the hydrogen was evaporated from the matrix prior to photolysis; the behavior of $HCo(CO)_4$ upon photolysis then matched its behavior in pure argon. Because the rate of loss of $HCo(CO)_4$ in a hydrogen-containing matrix so nearly approximates the rate of loss in a ^{13}CO-containing matrix, it is reasonable that the hydrogen reacts with $HCo(CO)_3$, the presumed intermediate in the photoinduced isotope exchange. Also, it is reasonable that only a single photon is required to effect the process. Thus, the oxidative addition (vide infra) of H_2 on $HCo(CO)_3$ appears to be a thermal process even at the low temperature of the matrix.

The spectra shown in Figure 1a,b,d are typical of what has been observed for hydrogen-containing matrices. Figure 1a shows the matrix of $HCo(CO)_4$ prior to photolysis. After 5 min of photolysis with a low-pressure mercury lamp the spectrum shown in Figure 1b results. Figure 1c shows the result of photolyzing a deuterium-doped matrix. New bands appear in Figure 1b at 2099.5, 2042.6, 2021, 2004, and 1994.8 cm^{-1}. Of these, the latter two decline in intensity as the matrix is exposed to the visible emissions of the Nernst glower (Figure 1d). This behavior suggests that the species that is responsible for these two absorptions is coordinatively unsaturated.[7] In fact, the band at 1994.8 cm^{-1} is nearly at the same position as a band assigned to $HCo(CO)_3$ in pure argon.[6]

Of the other three bands, those that appear at 2100 and 2043 cm^{-1} probably belong to the same species because their relative intensities are nearly the same in a number of spectra. The band at 2021 cm^{-1} cannot be well correlated because the band overlaps

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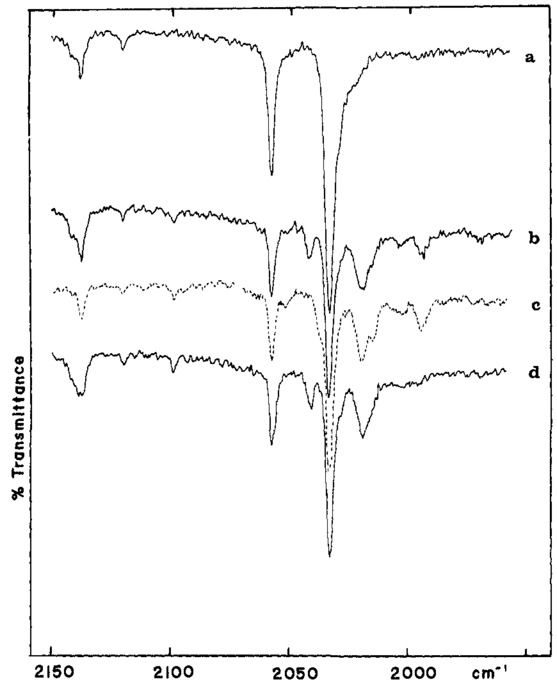

Figure 1. Infrared spectra of an argon matrix of $HCo(CO)_4$ containing 10 mol % of H_2 on liquid-helium-cooled NaCl: (a) immediately after deposit; (b) after 5 min of photolysis with a low-pressure mercury lamp; (c) after 5 min of photolysis of a similar matrix containing 10 mol % D_2; (d) after 25 min of exposure to the full emission of the Nernst glower.

absorptions due to $Co(CO)_4$. When deuterium-containing matrices of $HCo(CO)_4$ are photolyzed, the band at 2043 cm^{-1} does not appear. Rather, a band at 2038.3 cm^{-1} is observed as a shoulder on the principal absorption of $HCo(CO)_4$. The normal mode which affords the absorption at 2038.3 cm^{-1} undoubtedly correlates to the mode that absorbs at 2042.6 cm^{-1} in the hydrogen-containing matrix. The shift in the carbonyl modes upon deuteration is a well-known phenomenon among the hydrides.[8] Also, as deuterium-containing matrices of $HCo(CO)_4$ are photolyzed, a minor band grows in at 2052.5 cm^{-1}, which can be assigned to the low-frequency A_1 mode of $DCo(CO)_4$.[6] At the same time the intensity ratio of the low-frequency A_1 mode of $HCo(CO)_4$ to its E mode declines. The modes of E symmetry of both $HCo(CO)_4$ and $DCo(CO)_4$ appear at the same frequency. These data are consistent with isotope exchange between $HCo(CO)_4$ and D_2.

The behavior of $HCo(CO)_4$ in hydrogen-containing matrices is consistent with the following scheme:

$$HCo(CO)_4 \overset{254\ nm}{\rightleftharpoons} HCo(CO)_3 + CO$$

$$HCo(CO)_3 + H_2 \underset{254\ nm}{\rightleftharpoons} H_3Co(CO)_3$$

The bands at 2100 and 2043 cm^{-1} are assigned to the trihydride of cobalt tricarbonyl. If the band at 2021 cm^{-1} also belongs to the same species, then the $H_3Co(CO)_3$ is a meridional isomer analogous to $H_3Co(PPh_3)_3$.[9] The evidence points to the oxidative addition of hydrogen because (1) isotope exchange implies the hydrogen atom of the hydride becomes equivalent to those of the incoming hydrogens, (2) added deuterium perturbs the carbonyl modes in a similar fashion to other hydrides, (3) the frequencies of the carbonyl modes are similar to other coordinatively saturated cobalt carbonyls, and (4) the bands due to $H_3Co(CO)_3$ do not decline when the matrix is exposed to the visible radiation of the glower. On the other hand, $Co(CO)_4$ does not appear to react with H_2 under the same conditions. In CO matrices, the only observed product is $Co(CO)_4$, even in the presence of hydrogen.

The identification of another cobalt carbonyl hydride need not shake the currently held mechanisms for oxo chemistry.[10] $H_3Co(PPh_3)_3$ is readily decomposed in CO-containing atmospheres, and the same chemistry is suggested for $H_3Co(CO)_3$.[11] As $HCo(CO)_4$ is rarely handled except in CO atmospheres, $H_3Co(CO)_3$ may be present in inconsequential amounts. High-pressure studies of cobalt carbonyls by Whyman[12] and by Vidal and Walker[13] gave no evidence for $H_3Co(CO)_3$ although Whyman's study of iridium carbonyls did show the formation of a trihydridoiridium complex in a pure hydrogen atmosphere.[14]

Registry No. $H_3Co(CO)_3$, 81875-87-8; $HCo(CO)_4$, 16842-03-8.

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Photochemistry of Saturated Hydrocarbons. Mechanistic Changes as a Function of Methyl Substitution in the Photosensitized Reactions of the Tricyclo[4.1.0.0^{2,7}]heptyl System

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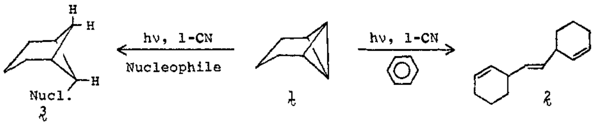
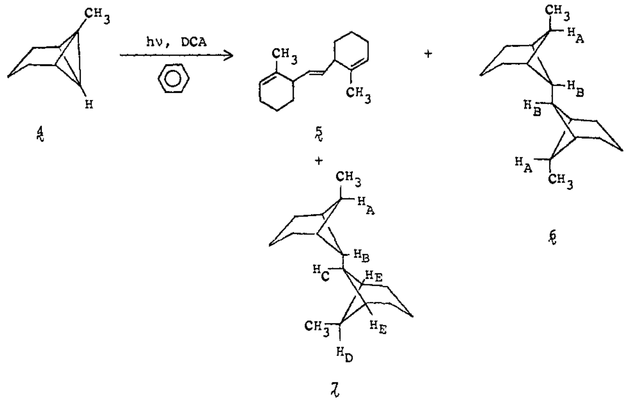
Received February 1, 1982

Recently, we reported an unprecedented series of photoinduced transformations of the saturated hydrocarbon tricyclo[4.1.0.0^{2,7}]heptane (**1**).[2] In the absence of nucleophiles, irradiation



of a solution of **1** and the photosensitizer 1-cyanonaphthalene (1-CN)[3] gave the dimer **2**, while in the presence of nucleophiles (i.e., methanol, water, cyanide ion) only **3** was obtained. We now report that methyl substitution on the tricyclo[4.1.0.0^{2,7}]heptyl skeleton can dramatically alter the paths of the photoinduced reactions of this hydrocarbon.

Irradiation of **4** in benzene containing 9,10-dicyanoanthracene



(DCA) through Pyrex with a 450-W medium-pressure Hanovia lamp for 8 h gave a mixture of **5** (17%), **6** (16%), and **7** (5%), in contrast to the 90% of **2** obtained from **1**. The structure of **5**

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