by silylation with *tert*-butyldimethylsilyl chloride (TBDMSCl) at room temperature afforded the 3-TBDMS ether **14** (mp 230–233 °C) in good yield. Fortunately, each of the three hydroxy groups in the 1,3,27-triol **13** could be distinguished, because the primary hydroxy group at C_{27} was not silylated under this condition probably due to the steric effect. Oxidation of **14** with *m*-CPBA to the sulfoxide followed by desulfenylation gave the unsaturated δ-lactone **15** (mp 197–198 °C), which had the same side-chain moiety as those of jaborosalactones.

The final problem of the construction of the A:B rings was accomplished as follows. Selective protection of the hydroxy group at C_{27} with methoxyethoxymethyl chloride (MEMCl) was followed by oxidation with pyridium dichromate (PDC) at C_1 to afford **16**, which was transformed into the 2,5-dien-1-one **17** in four steps. Epoxidation of **17** with *m*-CPBA gave a 1:2.5 mixture of two isomeric 5,6-epoxides, and subsequent separation by preparative TLC gave jaborosalactone A (**1a**) as the minor and less polar $5\beta,6\beta$-epoxide. Treatment of the major and more polar $5\alpha,6\alpha$-epoxide **18**[13] (mp 254–256 °C) with 3% perchloric acid yielded jaborosalactone D (**1c**). The reported isomerization of **1a** with base[4a] or dehydration of **1c** with *p*-toluenesulfonic acid gave jaborosalactone B (**1b**). The physical and spectral data of the synthesized samples were identical with the published data.[4] In addition, ^{1}H NMR,[15] HPLC, and CD data comparison of synthetic and natural materials of jaborosalactone A and B[16] showed no differences.

Acknowledgment. This research was supported by Grants in Aid (No. 521309) from the Ministry of Education of Japan.

Registry No. 1a, 5788-94-3; **1b**, 6105-16-4; **1c**, 19891-82-8; **2**, 566-77-8; **3**, 66875-12-5; **4**, 66875-21-6; **5**, 81426-78-0; **6a**, 81426-79-1; **6b**, 81897-53-2; **7**, 81874-38-6; **8**, 81426-80-4; **9**, 81426-81-5; **10**, 81874-39-7; **11a**, 81426-87-1; **11b**, 81426-82-6; **12a**, 81874-40-0; **12b**, 81874-45-5; **13**, 81874-41-1; **14**, 81967-91-1; **15**, 81874-42-2; **16**, 81874-43-3; **17**, 81874-44-4; **18**, 81939-02-8; $BrCH_2COBr$, 598-21-0.

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(15) We thank Dr. M. Fukui, The Institute of Physical and Chemical Research, for measurement of ^{1}H NMR (400 MHz) spectra.

(16) We express our appreciation to Professor I. Kirson, The Hebrew University of Jerusalem, for sending us the authentic samples of jaborosalactone A and B.

Bis(2,4-dimethylpentadienyl)titanium: An "Open Titanocene"

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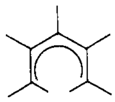
Received November 6, 1981

Two of the most useful ligands in organometallic chemistry are the closed five-membered cyclopentadienyl ligand and the open three-membered allyl ligand.[1] Very much neglected has been the chemistry of the related open five-membered pentadienyl ligand (I).[2] Various considerations have led us to the conclusion that



I

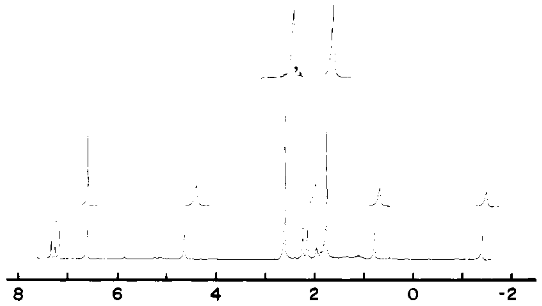


Figure 1. ^{1}H NMR spectra of $(2,4\text{-}C_7H_{11})_2Ti$ at −73 °C (below) and room temperature (above) in toluene-d_8.

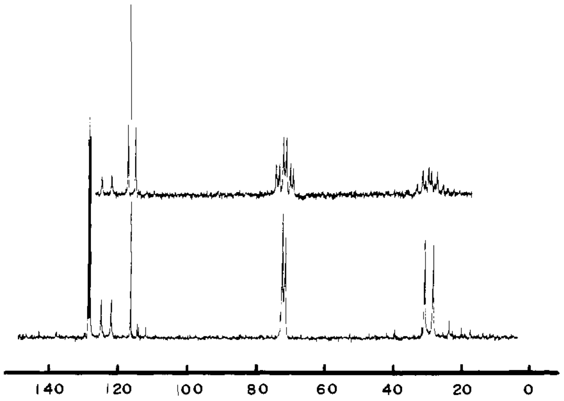


Figure 2. Proton-decoupled (below) and -coupled (above) ^{13}C NMR spectra of $(2,4\text{-}C_7H_{11})_2Ti$ at room temperature in benzene-d_6.

such a ligand should be capable of imparting both stability and catalytic activity into its metal complexes, and as a result we have been pursuing the chemistry of such systems.[3] Of initial interest have been bis(pentadienyl)metal complexes, which may be regarded essentially as "open metallocenes". Such complexes should allow detailed physical and chemical comparisons between the pentadienyl and cyclopentadienyl ligands, as well as providing a great deal of information for open-ligand systems (e.g., allyl) in general, which is not available primarily due to the very low stabilities of most homoleptic metal–allyl complexes. Thus, we have already reported such open sandwich compounds of vanadium, chromium, manganese, and iron.[3] However, perhaps the most intricate metallocene chemistry has been exhibited by titanium, for which the simple sandwich structure $Ti(C_5H_5)_2$ is well known to be quite unstable relative to various other (often extremely reactive) forms, which may contain fulvalene, $\eta^1,\eta^5\text{-}C_5H_4$, hydride, and perhaps other ligands as well.[4] Indeed, even decamethyltitanocene possesses only limited stability.[5] Because of the rich variety of chemistry demonstrated by the titanocene systems, it was anticipated that the chemistry of open-titanocene

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(1) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(2) Some examples: (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551. (c) Rienacker, R.; Yoshiura, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 677. (d) Krüger, C. *Ibid.* **1969**, *8*, 678. (e) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189.

(3) (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 1120. (c) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708. (d) Ernst, R. D.; Campana, C. F.; Wilson, D. R.; Liu, J.-Z., to be submitted for publication. (e) Bohm, M. C.; Eckert-Maksić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699.

(4) (a) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301. (b) Brintzinger, H. H.; Bercaw, J. E. *Ibid.* **1970**, *92*, 6182. (c) Bercaw, J. E.; Brintzinger, H. H. *Ibid.* **1971**, *93*, 2045. (d) Marvich, R. H.; Brintzinger, H. H. *Ibid.* **1971**, *93*, 2046. (e) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *Ibid.* **1972**, *94*, 1219. (f) Alt. H.; Rausch, M. D. *Ibid.* **1974**, *96*, 5936. (g) Guggenberger, L. J.; Tebbe, F. N. *Ibid.* **1976**, *98*, 4137. (h) Pez, G. P. *Ibid.* **1976**, *98*, 8072. (i) Pez, G. P.; Kwan, S. C. *Ibid.* **1976**, *98*, 8079. (j) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203. (k) Armor, J. N. *Ibid.* **1978**, *17*, 213. (l) Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1972**, 481. (m) Peng, M.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1978**, *26*, 231. (n) Pez, G. P.; Armor, J. N. In "Advances in Organometallic Chemistry"; West, R., Stone, F. G. A., Eds.; Academis Press: New York, 1981; Vol. 19, p 1.

(5) (a) The compound actually exists in equilibrium with $(\eta^5\text{-}C_5(CH_3)_5)(\eta^6\text{-}C_5(CH_3)_4CH_2)TiH$ and decomposes slightly above room temperature.[5b] (b) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

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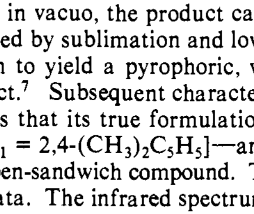
systems would likewise prove interesting. In particular, the large size of a pentadienyl ligand would seem of benefit in stabilizing electron-deficient complexes, and the lack of aromatic character might prove a hindrance to ligand-metalation processes. We therefore set out to investigate the nature of possible open titanocene compounds using the convenient 2,4-dimethylpentadienyl anion as a ligand source.

The reaction of titanium dichloride, prepared in situ by the magnesium reduction of titanium tetrachloride, with the potassium salt of the 2,4-dimethylpentadienyl anion under nitrogen in THF at −78 °C leads to the formation of a deep green solution.[6] After removal of solvent in vacuo, the product can be extracted with pentane and purified by sublimation and low-temperature (−78 °C) crystallization to yield a pyrophoric, volatile, deep green low-melting product.[7] Subsequent characterization of this material demonstrates that its true formulation is that of $Ti(2,4\text{-}C_7H_{11})_2$ [$2,4\text{-}C_7H_{11} = 2,4\text{-}(CH_3)_2C_5H_5$]—an unperturbed, divalent, 14-electron open-sandwich compound. This conclusion rests on the following data. The infrared spectrum of this compound is nearly identical with that of the well characterized $V(2,4\text{-}C_7H_{11})_2$ counterpart.[3b] A room-temperature mass spectrum of this compound displayed parent-related peaks at *m/e* 238 (16%), 239 (3.9%), and 240 (1.6%). The observed relative ratios of these peaks are in agreement with calculated isotopic ratios by assuming *m/e* = 238 as the parent peak, corresponding to $TiC_{14}H_{22}^+$. No evidence of hydride or any other extraneous ligand could be observed.[8] The product is diamagnetic, as demonstrated by magnetic susceptibility measurements using the Evans solution NMR method.[9] An isopiestic molecular weight determination in pentane proves the compound to be monomeric.[10] ^{1}H and ^{13}C NMR data have been obtained and are shown in Figures 1 and 2. Notably, seven resonances are observed in the ^{1}H NMR spectrum, while only four were present in $Fe(2,4\text{-}C_7H_{11})_2$.[3a] It is therefore apparent that the two C_7H_{11} ligands in $Ti(2,4\text{-}C_7H_{11})_2$ are equivalent but lack the mirror plane of symmetry perpendicular to the idealized ligand plane.



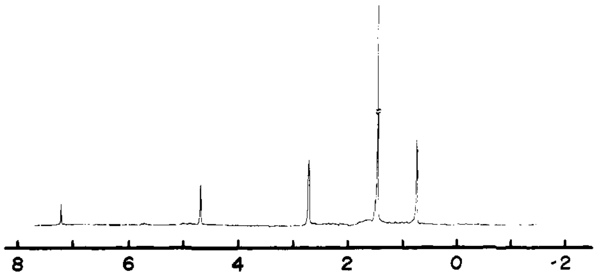


Figure 3. ^{1}H NMR spectrum of $(2,4\text{-}C_7H_{11})_2Ti(CO)$ at room temperature in benzene-d_6.

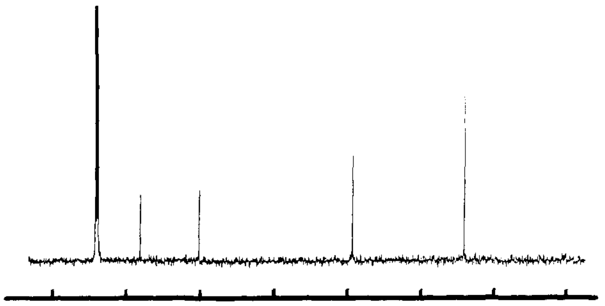
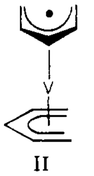


Figure 4. ^{13}C NMR spectrum of $(2,4\text{-}C_7H_{11})_2Ti(CO)$ at room temperature in benzene-d_6. Not shown is the ^{13}CO resonance at 255.9 ppm.

The room-temperature ^{1}H NMR spectrum evidences substantial broadening of all but the H_c resonances clearly due to a process in which the perpendicular mirror plane is becoming restored on the NMR time scale. Similarly, the ^{13}C NMR spectrum displays seven resonances at room temperature, again indicative of the absence of the perpendicular mirror plane. The general order of resonances (quaternary > CH > CH_2 > CH_3) follows the same pattern as $Fe(2,4\text{-}C_7H_{11})_2$ and is readily confirmed by the proton-coupled spectrum.[11] Again, substantial broadening of all but the CH resonance indicates the restoration of the perpendicular mirror plane by thermal motion. By 56 °C the quaternary resonances have become a single very broad peak, the CH resonance remaining sharp, the CH_2 resonances becoming a slightly broadened singlet, and the CH_3 resonances becoming a broad singlet. Noteworthy is the apparent lack of decomposition observed in the period (1 h) required for high-temperature data accumulation. More detailed variable-temperature studies of this compound are in progress. It is quite clear, however, that the conformational nature of this compound differs markedly from that of $Fe(2,4\text{-}C_7H_{11})_2$, and recent data allow a reasonable explanation of these observations. Molecular orbital calculations have indicated that δ bonding appears to be the origin of the preference of an eclipsed conformation for the bis(pentadienyl)iron systems,[3e] as evidenced by the solid-state structure of $Fe(2,4\text{-}C_7H_{11})_2$[3a] as well as the theoretical calculations themselves. In the related $V(2,4\text{-}C_7H_{11})_2$ compound, however, a staggered conformation is observed in the solid state (II). The apparent reason for this difference can be traced to the differing electron configuration for the iron and vanadium compounds, particularly the presence of only one unpaired electron in low-spin $V(2,4\text{-}C_7H_{11})_2$.[12] If



II

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(6) (a) The preparation of the apparently divalent $TiCl_2$ complex was carried out in a fashion similar to that for $VCl_2(THF)_2$, substituting Mg for Zn.[6b] The blackish solution and precipitate appeared similar to the reported $TiCl_2(THF)_2$.[6c] Best yields of $Ti(C_7H_{11})_2$ seem to be obtained when the mixture is kept at −78 °C for at least 4 if not more hours and then slowly warmed to room temperature. All reactions and manipulations were carried out under nitrogen. (b) Köhler, F. H.; Prössdorf, W. *Z. Naturforsch., B* **1977**, *32B*, 1026. (c) Fowles, G. W. A.; Lester, T. E.; Walton, L. A. *J. Chem. Soc. A* **1968**, 1081.

(7) The product is isolated as a liquid. Repeated recrystallization does increase the melting point somewhat, but even single crystals melt below room temperature. It can be noted that $V(2,4\text{-}C_7H_{11})_2$ sublimes at ca. 40 °C onto a 20 °C cold finger in vacuo, yielding a liquid product that crystallizes on standing for a few days.

(8) (a) Obtaining accurate analytical data has apparently been hampered by the extremely pyrophoric nature of this compound and its rather sticky consistency. Anal. Calcd for $C_{14}H_{22}Ti$: C, 70.58; H, 9.31; N, 0.00. Found: C, 68.92; H, 9.43; N, 0.00. The elemental composition has been also verified by high-resolution mass spectroscopy: calcd 238.1201; found, 238.1215. (b) The absence of coordinated N_2 has been verified by several observations. First, the Raman spectrum completely lacks any band corresponding to $\nu_{N\equiv N}$. In addition, the mass spectrum of the volatile compound contains no ion peaks due to a nitrogen adduct, and no color changes can be observed on sublimation (cf., $(C_5(CH_3)_5)_2Ti$[4c]). Reaction with CO, 2,2′-dipyridine, and diphenylacetylene takes place immediately without release of N_2. The great differences in NMR patterns for $Ti(2,4\text{-}C_7H_{11})_2$ vs. $Ti(2,4\text{-}C_7H_{11})_2(CO)$ also argue against N_2 coordination. (c) Reaction with equimolar methyl iodide leads to slow decomposition of some of the product. Only traces of methane are observed by gas chromatography (ca. 2% conversion from CH_3I after 2 h). Reaction with an excess of methyl iodide leads to slow but complete decomposition, again leading to the formation of only relatively small quantities of methane.

(9) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(10) Found, 215.

(11) The resonances for the iron compound appear at 99.7, 93.9, 51.1, and 26.8 ppm, while those for the titanium compound appear at 125.1, 122.3, 116.6, 72.8, 71.9, 31.5, and 29.0 ppm. For comparison, at 56 °C the four resonances are observed at 123.5, 116.6, 72.5, and 29.9 ppm. All positions were obtained by use of C_6D_6 as internal standard and indirectly referenced to tetramethylsilane ($\delta(C_6D_6)$ 128.5 vs. Me_4Si).

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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(1) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410–2412.

(2) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393–7394. Barrett, P. H.; Pasternak, M.; Pearson, R. G. *Ibid.* **1979**, *101*, 222–223.

(3) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574–1575.

(4) Ault, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 3480–3484.

(5) Sweany, R. L. *Inorg. Chem.* **1982**, *21*, 752–756.

(6) An earlier report (Wermer, P.; Ault, B. S.; Orchin, M. J. *Organomet. Chem.* **1978**, *162*, 189–194) of the assignment of the species observed in argon matrices proved to be in error: Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3512–3516.

(7) Muskovits, M.; Ozin, G. A. "Cryochemistry"; Wiley-Interscience: New York, 1976.

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