NMR techniques will become of wider interest for the comprehensive study of fluxional organometallic molecules.

Acknowledgments. F.S. thanks the Max-Planck-Gesellschaft for the grant of a stipend. R.B. thanks Prof. Dr. K. Jonas for drawing his attention to the investigations of the haptotropic rearrangements mentioned in ref 28–30.

Registry No. 1, 121987-59-5; 2, 121987-60-8.

Photolysis of Tetracarbonylnickel in Dihydrogen-Containing Matrices: Evidence for the Formation of a Complex of Molecular Hydrogen

Ray L. Sweany,* Michael A. Polito, and Antoni Moroz

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received January 11, 1989

When H_2/Ar matrices of $Ni(CO)_4$ are irradiated by ultraviolet light, new infrared bands are detected that are assigned to a complex of molecular hydrogen, $Ni(CO)_3(H_2)$. The complex is characterized by two carbonyl stretching vibrations at 2033.1 and 2109.8 cm^{-1}. These bands and those of isotopically labeled molecules were used to calculate an anharmonic, energy factored force field with C_{3v} symmetry. The carbonyl stretching force constant of 1711.4 N·m^{-1} is intermediate between that of $Ni(CO)_4$ and $Ni(CO)_3$, an indication that the dihydrogen is probably coordinated as opposed to having been oxidatively added. The force field was used to calculate the OC–Ni–CO bond angle from the observed intensities of the carbon-12 isotopomer. The carbonyl portion of the molecule can be viewed as approximately tetrahedral, with the three remaining carbonyls more splayed than would be found in a tetracarbonyl complex. The angle between carbonyls is 115.6 ± 1.0°. $Ni(CO)_3(H_2)$ loses H_2 with photons of the same energy as those which are used in its production. Thus, the quantity of $Ni(CO)_3(H_2)$ that could be formed was limited. None of the vibrational features that are associated with the hydrogen were observed by FTIR. This failure probably results from our inability to form large quantities of the complex and the inherent weakness of the hydrogen-containing vibrational modes. The hydrogen is probably bonded in an η^2 fashion in order for the H–H stretch to be so weak.

Introduction

Since the first published description of a complex of molecular hydrogen,[1] a number of complexes have been characterized, some of which are stable at room temperature.[2] Complexes of hydrogen have readily been formed in inert-gas matrices by the ultraviolet irradiation of stable 18-electron precursors in the presence of dihydrogen.[3-5] Hydrogen concentrations as high as 25 mol % have been achieved in matrices. Thus, there is a high probability that every coordinatively unsaturated complex that is formed has at least one molecule of hydrogen nearby. Positive identification of the mode of bonding is made difficult because of the low intensity and broadness of some of the infrared modes which are most diagnostic, in particular, the H–H and the M–H_2 stretching modes of coordinated dihydrogen and the M–H stretching mode of a normal hydride.[2,6] In previous matrix studies, and in this report, the behavior of the carbonyl modes are used to differentiate between hydrogen that has oxidatively added and that which has coordinated dihydrogen. Hydrogen withdraws less electron density from the metal when it coordinates than when it oxidatively adds, and the carbonyl modes can serve as a measure of this flow of metal electron density. In extreme cases, it is easy to differentiate between the modes of bonding, although it is unclear how much a perturbation dihydrogen can cause and still be considered coordinated.[4] Here, we report the formation of $Ni(CO)_3(H_2)$ in photolyzed matrices of $Ni(CO)_4$. An earlier report claiming the oxidative addition of hydrogen was based on early experiments in which a band was observed in the region of normal metal–hydride deformations.[7] The observation of this band could not be repeated in subsequent experiments.

Results and Discussion

$Ni(CO)_3$ has been formed in matrices by the irradiation of $Ni(CO)_4$. Two absorptions were observed at 2067.4 and 2014.5 cm^{-1}.[8] The relative intensity of the two modes vary considerably as a function of the matrix. Subsequently, the high-frequency band was shown to be due to near-neighbor interactions with other $Ni(CO)_4$ moieties.[9] Only a single absorption was observed when $Ni(CO)_3$ was formed from Ni atoms and CO.[10] Thus, $Ni(CO)_3$ can be presumed to be planar with only a single infrared-active carbonyl vibration. When H_2 is present in the matrix, two new bands at 2109.8 and 2033.1 cm^{-1} result from the irradiation of the matrix by 254-nm light. They are assigned to a new species which will be referred to as I. A typical spectrum

---

[1] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, R. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984,** *106,* 451–452.

[2] Kubas, G. J. *Acc. Chem. Res.* **1988,** *21,* 120–128.

[3] Sweany, R. L. *J. Am. Chem. Soc.* **1985,** *107,* 2374–2379.

[4] Sweany, R. L. *J. Am. Chem. Soc.* **1986,** *108,* 6986–6991.

[5] Sweany, R. L.; Russell, F. N. *Organometallics* **1988,** *7,* 719–727.

[6] Sweany, R. L.; Moroz, A. *J. Am. Chem. Soc.,* in press.

[7] Sweany, R. L. *Abstr. Pap., Am. Chem. Soc.* **1985,** INOR 152.

[8] Rest, A. J.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1969,** 1026.

[9] Poliakoff, M., unpublished results revealed in reviewer comments.

[10] DeKock, R. L. *Inorg. Chem.* **1971,** *10,* 1205–1211.

0276-7333/89/2308-2305$01.50/0

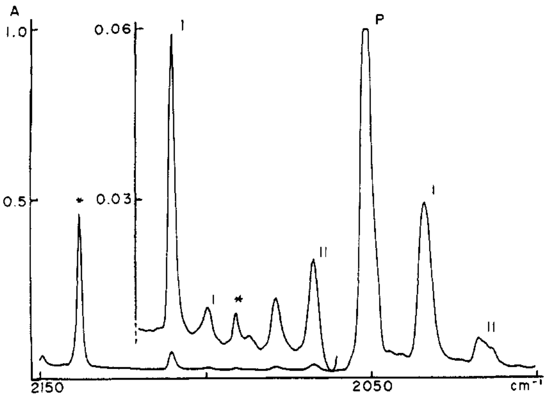

Figure 1. (a) Spectrum of 0.3% $Ni(CO)_4$ in 18% H_2 in argon which was deposited for 34 min after which the matrix was irradiated for 4 h with two low-pressure mercury lamps, 1 cm in length. The spectrum was the average of 100 scans made on the FTIR with 1 cm^{-1} resolution. The band marked by P is due to $Ni(CO)_4$; those marked by I and II are due to $Ni(CO)_3(H_2)$ and $Ni(CO)_3$, respectively. Asterisks mark bands due to CO, most of which were present prior to irradiation.

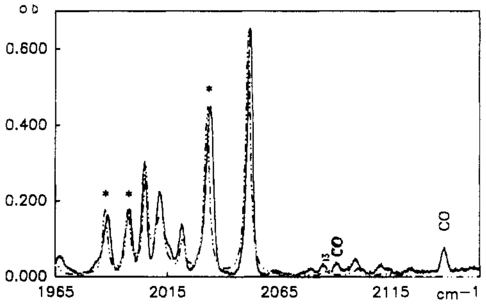

Figure 2. Solid line is a spectrum of an argon/H_2(19%) matrix of 0.1% isotopically labeled $Ni(CO)_4$ after 5.5 h of irradiation. The spectrum of I alone could not be successfully obtained by spectral subtraction. Therefore, the spectra of both $Ni(CO)_4$ and $Ni(CO)_3(H_2)$ were fit. The enrichment was determined by inspection of the unphotolyzed matrix (70-min deposit). The ratios of $^{13}CO/^{12}CO = 0.7$ and $^{13}CO/^{13}C^{18}O = 5$ were used to fit both spectra. The calculated spectra were added together in order to give the spectrum shown by the dashed line. Bands that are marked with an asterisk are substantially due to $Ni(CO)_3(H_2)$.

is shown Figure 1. Being made aware that the $Ni(CO)_3$ spectrum becomes perturbed by near neighbors at fairly dilute concentrations,[9] a matrix was formed from 0.02% $Ni(CO)_4$ and 19% H_2 in argon. The two features assigned to I appeared with the same relative intensities as are observed with higher concentrations of $Ni(CO)_4$. Thus, the formation of I only requires one molecule of $Ni(CO)_4$. Concomitant with the growth of bands due to I is the growth of a band at 2139 cm^{-1} which is due to free, uncoordinated CO. From this evidence, we conclude that I is formed from a coordinatively unsaturated nickel complex and dihydrogen. Because Ar/H_2 matrices of $Ni(CO)_4$ give no evidence of an ESR spectrum, we assume the new product must result from either the oxidative addition of both hydrogen atoms or the coordination of dihydrogen to nickel.[11]

The stoichiometry of I can be deduced from an analysis of the spectra. That only two bands are assigned to I suggest that it is either a tricarbonyl fragment with 3-fold symmetry or a bent dicarbonyl. If I were to be a dicarbonyl, then the relatively high frequency of the absorptions would suggest that hydrogen had oxidatively added. Otherwise, the frequencies of a $Ni(CO)_2(H_2)_x$ would be expected at lower frequency than observed for $Ni(CO)_3$. These expectations are based on the presumption that dihydrogen withdraws less electron density from the metal when it coordinates compared to when it oxidatively adds. If I were a dicarbonyl fragment to which H_2 had oxidatively added, then one would expect to be able to observe the M–H deformation modes between 700 and 900 cm^{-1}.[12] These modes can be as much as 10% of the intensity of the carbonyl modes. However, there is no evidence of absorptions in this region. Thus, I is probably a complex of H_2 derived from $Ni(CO)_3$. We offer several other reasons for concluding that three carbonyl groups remain attached to nickel. (1) Ligand-loss processes usually occur sequentially in matrices, and one would expect to observe some type of tricarbonyl feature initially, (2) the yield of $Ni(CO)_3$ is suppressed when hydrogen is present, and (3) a force field which presumes C_{3v} symmetry fits the positions of bands due to isotopomers which are labeled with carbon-13 (vide infra). When D_2 or HD is present, the spectrum of I is not altered within experimental error. This is not unexpected; the mass of hydrogen has rarely shown a detectable affect on the carbonyl modes.[3,6,19]

Prolonged irradiation of $Ni(CO)_4$ in H_2-containing matrices does not completely convert $Ni(CO)_4$ to products. No additional peaks appear in response to prolonged irradiation, either. Rather, a photostationary state is established after which no additional conversion occurs. All absorptions in the carbonyl region have been assigned except for two minor peaks that are observed at 2086 and 2079 cm^{-1}. The intensities of these bands are similar to the intensities of the carbon-13 isotopomer bands of $Ni(CO)_3(H_2)$ at natural abundance, and it is difficult and probably unnecessary to speculate as to their identity. The following scheme is consistent with the behavior of $Ni(CO)_4$.

$$Ni(CO)_4 \xrightarrow{254\ nm} Ni(CO)_3 + CO \tag{1}$$

$$Ni(CO)_3 + CO \rightarrow Ni(CO)_4 \tag{2}$$

$$Ni(CO)_3 + H_2 \rightarrow \underset{I}{Ni(CO)_3(H_2)} \tag{3}$$

$$Ni(CO)_3H_2 \rightarrow Ni(CO)_3 + H_2 \tag{4}$$

Because of the photosensitivity of $Ni(CO)_3(H_2)$, large quantities could not be obtained and no band could be assigned to any of the hydrogen-containing vibrational coordinates using H_2, HD, or D_2. The bands must be quite weak for them to have escaped detection. In spite of the photostationary state, the maximum intensity that has been observed for the totally symmetric A_1 vibration of the carbonyls was 0.4 optical density unit. With the assistance of FTIR, absorptions 100 times less intense could easily be detected. The D–D stretch of $Cr(CO)_5(D_2)$ is more narrow and less perturbed than either the H–H or the H–D stretch.[6,14] By analogy, the D–D stretch of $Ni(CO)_3(D_2)$ should be more readily detected. If adequate amounts of $Ni(CO)_3(D_2)$ had been formed in our experiments, then the D–D stretch must be buried in the region of atmospheric CO_2 absorptions between 2390 and 2320 cm^{-1}. The D–D stretch of D_2 coordinated on a nickel surface appears at 2307 cm^{-1},[15] which is at a position just

---

[11] H atoms react with $Ni(CO)_4$ to give $HNi(CO)_3$ which has been detected by ESR spectroscopy. Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1984**, *81*, 5775–5778.

[12] Jesson, J. P. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Deker: New York, 1971; pp 75–201.

[13] Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466–468.

[14] Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27–30.

Table I. Observed and Calculated Positions of Carbonyl Bands of $Ni(CO)_3(H_2)$

molecule	obsd	calcd
$Ni(^{12}CO)_3(H_2)$	2109.8	2110.7
	2033.1	2032.5
$Ni(^{12}CO)_2{}^{13}CO(H_2)$	2099.6	2099.8
	2033.1[b]	2032.5
	1997.4	1997.4
$Ni^{12}CO(^{13}CO)_2(H_2)$	2085.2	2086.2
	2010.7	2010.5
	1987.5	1987.2
$Ni(^{13}CO)_3(H_2)$	2063.0	2063.6
	1987.5[b]	1987.2

[a] The accuracy of positions is estimated to be ±1.0 cm^{-1} when bands are well resolved. [b] Position is obscured by another band of another isotopomer.

Table II. Force Constants Used in an Energy-Factored Force Field (N/m)

	$Ni(CO)_3$	$Ni(CO)_3(H_2)$	$Ni(CO)_4$
$k_{C-O}{}^a$	1700		1723
$k_{C-O}{}^b$	1669.4 ± 1.7[c]	1711.4 ± 0.7	1732.1 ± 0.2[d]
$k_{C-O,C-O}{}^b$	28.4 ± 1.1[c]	43.6 ± 0.5	34.0 ± 0.1[d]

[a] Taken from ref 16. The fit is described as a Cotton–Kraihanzel force field, details of which are lacking. These values should be compared to those calculated by DeKock for planar $Ni(CO)_3$ which was formed from Ni atoms and CO. k_{C-O} = 1700 N/m by assuming an interaction force constant of 57 N/m.[8] [b] This work. [c] Calculated by using 2076.8 and 2016.1 cm^{-1} for the most abundant isotopomer, only. It should be noted that the totally symmetric breathing mode has been activated by the presence of a nearby $Ni(CO)_4$. Therefore, this particle is not truly $Ni(CO)_3$. [d] Calculated from a least-squares fit of four frequencies. The force field was then checked for its ability to fit all other observations.

on the edge of a region in which observations of weak absorptions are very difficult. Neither the H–D or H–H stretch were detected. Rotational motions of the lighter isotopomers cause broadening and splitting in their respective stretching vibrations, making them harder to observe.[6,13,14]

Because of the anticipated low intensity of the dihydrogen-containing vibrational modes, our inability to observe them does not preclude I from being a complex of dihydrogen. There are two reasons for claiming that I is $Ni(CO)_3(H_2)$. The absence of any band that might be assigned to a M–H deformation mode of a normal hydride makes it difficult to claim that hydrogen had oxidatively added. Furthermore, the results of a energy-factored force field analysis also supports the assignment.

The force field analysis made use of data from carbon-13 isotopically labeled $Ni(CO)_3(H_2)$. If the unlabeled molecule has 3-fold symmetry, then there are only two unique force constants and the two absorptions of the carbon-12 isotopomer was sufficient to solve the force field. With this solution, the positions of the carbon-13 isotopomer bands were calculated with good accuracy, cutting short the sometimes laborious task of making and testing assignments. Finally, all observed frequencies were used to calculate the force constants that are reported in Table I. The good agreement between observed and calculated frequencies corroborates the structural and stiochiometric assignments.

The stretching force constant for $Ni(CO)_3(H_2)$ was found to be 1711.4 N m^{-1} intermediate between that of $Ni(CO)_4$ and $Ni(CO)_3$[16] (see Table II). The same ordering was observed for the force constants of $Cr(CO)_6$, $Cr(CO)_5(H_2)$, and $Cr(CO)_5$.[14] The dihydrogen of $Cr(CO)_5(H_2)$ is certainly bonded in a η^2 fashion. For contrast, the force constants for the carbonyl stretching vibration for $H_2Fe(CO)_4$ are much greater than those of either $Fe(CO)_5$ or $Fe(CO)_4$.[17] During oxidative addition, electron density is drawn off a metal, and this loss is recorded by the carbonyl ligands. The degree to which hydrogen can withdraw electron density from a metal and still retain its H–H bond is unclear. For example, the carbonyl force constants for $HWCp(CO)_2(H_2)$ are larger than for $HWCp(CO)_3$.[4] For I, there is less ambiguity because the carbonyl force constant of $Ni(CO)_4$ is significantly greater than that of I.

Morris has shown a good correlation between the stability of dihydrogen-containing complexes and the frequency of the N–N stretch of the complex formed by replacing H_2 by N_2.[18] The N–N stretch of 2264 cm^{-1} of $Ni(CO)_3N_2$[19] places I in a class of dihydrogen adducts that ought to be unstable at room temperature. Although our conclusions concerning the mode of attachment is in agreement with what can be predicted from Morris' survey, nothing from these experiments can allow an assessment of stability.

Dihydrogen dissociatively chemisorbs on nickel surfaces for the most part.[15] Recently, the H–H stretch was reported for dihydrogen on a Ni(510) surface that was nearly fully covered with adsorbed hydrogen atoms. It was supposed that the occasional dihydrogen molecules that were coordinated were situated on an edge. Although the orientation of the hydrogen cannot be inferred from these experiments, we note that two other complexes of hydrogen on a d^{10} transition-metal have been characterized as η^2 complexes. For both $Co(CO)_2NO(H_2)$ and $Fe(CO)(NO)_2(H_2)$, the H–H stretching vibration was broad which was thought to be consistent with a hydrogen that was rotating on the coordination site.[20] These complexes and $Ni(CO)_3(H_2)$ were modeled by using an extended Hückel calculation by Burdett et al.[21] The hydrogen was found to be η^2, analogous to what is exhibited by $W(PR_3)_2(CO)_3(H_2)$. An orbital which is largely $4p_z$ in character functions as an acceptor orbital, whereas the orbital which is largely due to the d_{z^2} is both filled and destabilized by the H–H σ orbital. This 4e repulsive interation might cause the hydrogen to prefer end-on coordination; this orientation would prevent any π interaction, however. In fact, the interaction of a filled d_π orbital on nickel with the hydrogen σ^* was found to be energetically more favorable than for an analogous interaction in $Cr(CO)_5(H_2)$. Palladium metal atoms, on the other hand, are claimed to exhibit both η^1 and η^2 coordination, suggesting that the repulsive interactions are more dominant.[22]

In order to calculate the bond angles in the $Ni(CO)_3$ fragment of I, areas were obtained from a spectrum by curve resolution. The ratio of areas for the E and A_1 vibrations was found to be 21.8 ± 1.9 for the all-$^{12}C^{16}O$ isotopomer, where the error statistic is twice the estimated standard deviation of the average over three determina-

---

(15) Martensson, A.-S.; Nyberg, C.; Andersson, S. *Phys. Rev. Lett.* **1986**, *57*, 2045–2048.

(16) Kündig, E. P.; McIntosh, D.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7234–7241.

(17) Sweany, R. L.; Owens, J. W. *J. Organomet. Chem.* **1983**, *255*, 327–334.

(18) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674–2683.

(19) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B., II *J. Am. Chem. Soc.* **1983**, *105*, 3898–3904. Rest, A. J. *J. Organomet. Chem.* **1972**, *40*, C76–C78.

(20) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547–2552.

(21) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054–3063.

(22) Ozin, G. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1986**, *108*, 3099–3100.

tions. Using the calculated force field for $Ni(CO)_3(H_2)$ and this ratio, the angle between the carbonyl ligands was found to be 115.6 ± 1.0°.[23] To further check, intensities were calculated for isotopically labeled $Ni(CO)_3(H_2)$ in two instances and compared with observed spectra. The extent of isotopic substitution was determined from a fit of the spectrum of $Ni(CO)_4$ before photolysis. The agreement was very good, particularly among those modes that were not totally symmetric. In doing this calculation we acknowledge that calculating bond angles for $M(CO)_n$ fragments can especially be in error if there are other π-bonding ligands attached to the metal.[24] The π bonding of hydrogen may not seriously affect the carbonyl intensities because we do not note any coupling of the modes as judged by isotope effects. Thus, the structure of the carbonyl fragment must be viewed as intermediate between trigonal and tetrahedral. To summarize discussions that have already occurred, the hydrogen probably bonds to this fragment in a η^2 fashion, making the observation of the the hydrogen-containing vibrational features difficult.

Experimental Section

Matrices were formed either by depositing a gas mixture which already contained $Ni(CO)_4$ or by subliming $Ni(CO)_4$ into a stream of matrix gas just prior to deposition at liquid-helium temperatures. One liter of a gas mixture containing $Ni(CO)_4$ was made by using Ar and hydrogen as diluent gases. These mixtures were made in a vacuum line which was pumped to 0.02 mmHg. To avoid contamination by residual atmospheres in the apparatus, the apparatus was flushed several times with argon. Typically, mixtures were made with 0.1 mol % of $Ni(CO)_4$ and concentrations of hydrogen between 10 and 20 mol %. Over the course of several hours, a dark deposit forms on the flask walls that is undoubtedly nickel metal formed by $Ni(CO)_4$ decomposition. Other than a band due to free CO, no peaks are noted in the carbonyl region of the infrared spectrum that can be attributed to other decomposition products of $Ni(CO)_4$.

Matrices were also formed by subliming $Ni(CO)_4$ into a matrix gas stream just prior to deposition. The temperature of the $Ni(CO)_4$ was maintained at close to −110 °C in order to assure a low doping level. When the rate of growth of peaks due to $Ni(CO)_4$ deposited in this manner are compared to those formed from gas mixtures, it is clear that the doping level is on the order of 0.1%. The infrared band due to $Ni(CO)_4$ was always symmetric and on the order of 4 cm^{-1} at half-height, also indicating that the sample was adequately isolated. Spectra were recorded by either a Beckman 4260 infrared spectrometer which is coupled to a Zenith Z-100 microcomputer or on a Perkin-Elmer 1760 Fourier Transform infrared spectrometer. Experimental details have been previously published.[5]

The methods used to obtain a energy-factored force field have been described elsewhere.[3] The ratio of intensities of the A_1 and E mode of the carbonyl stretches was measured after first fitting the band envelopes with a product function of Lorentzian and Gaussian line shapes. The areas of the fitted bands were calculated by a trapezoidal method.[5] The ratio of intensities at ν_{max} of the two absorptions observed for $Ni(CO)_3$ which was formed from $Ni(CO)_4$ varied considerably as a function of the matrix identity.[8] In order to guard against similar matrix effects in the spectrum of I, areas were measured of unresolved FTIR spectra in Ar and Kr matrices. The intensity ratio observed in Kr was within experimental error of those observed in Ar. Also, areas were obtained by similar procedures of unresolved FTIR spectra from matrices that ranged from 0.02% to 0.3% $Ni(CO)_4$ which were in good agreement with each other.

Acknowledgment. We gratefully acknowledge the helpful suggestions made by Dr. M. Poliakoff. Support for this work was provided by the donors of the Petroleum Research Fund, administrated by the American Chemical Society, and by the Research Council of the University of New Orleans. We wish to further acknowledge the Louisiana Quality Education Trust Fund, administered by the Louisiana Board of Regents, for funds for the purchase of the FTIR spectrometer.

Registry No. $Ni(^{12}CO)_3(H_2)$, 122382-64-3; $Ni(^{12}CO)_2{}^{13}CO(H_2)$, 122382-65-4; $Ni(^{13}CO)_3(H_2)$, 122382-66-5; $Ni(CO)_4$, 13463-39-3; H_2, 1333-74-0.

---

[23] M. Poliakoff, in evaluating this paper, has pointed out that there is a simple equation which allows the calculation of a bond angle from intensity data for a tricarbonyl fragment. The acute angle between the 3-fold axis and the carbonyl groups, T, is given by tan $(T) = \{I_e/I_a\}^{0.5}$ where I_e and I_a are the intensities of the E and A_1 modes, respectively. Application of this equation is in good agreement with the more empirically derived angle that we have calculated.

[24] Burdett, J. K. *Inorg. Chem.* 1981, *20*, 2607–2617.

Lithio(diphenylphosphino)methane–Tetramethylethylenediamine: Crystal Structure and NMR Studies of a Coordinatively Unsaturated, Monomeric Organolithium

Gideon Fraenkel* and William R. Winchester

Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus Ohio 43210

P. G. Williard

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Received January 19, 1989

A crystal structure determination on the tetramethylethylenediamine (TMEDA) adduct of lithio(diphenylphosphino)methane has shown it to be a *monomeric* species, with tricoordinate lithium *terminally* bonded to the methylene group. The results of ^{13}C NMR studies are consistent with this; only one species is observed at all temperatures, presumably the monomer. ^1H NMR studies reveal that the α-methylene protons are nonequivalent at the lowest temperatures, consistent with the observed crystal structure and indicating slow inversion at carbon.

Organolithium compounds are important reagents in both organic and inorganic synthesis whose structures and aggregation states continue to surprise and confound researchers.[1] Initial studies revealed that organolithiums

0276-7333/89/2308-2308$01.50/0