Organometallics **1987,** *6,* 391–397

A common reduction process at negative potentials is observed on the reverse scan of cyclic voltammetry either after a two-electron oxidation or under conditions where process 1 is an ECE-type mechanism. This process presumably corresponds to a two-electron reduction of a rearranged seven-coordinate oxidation state(II) complex to $M(CO)_3$(steroid).

Reaction Scheme III demonstrates a proposed mechanism for a process involving formation of a rearranged steroid with two competing pathways. Quantitative recovery of the initial steroid and not a modified steroid is observed experimentally and would be expected by the proposed mechanism when the 18-electron oxidation state (II) complex decomposes.

A number of mechanistic pathways for the oxidation of arene metal carbonyls complexes have been reported. In noncoordinating solvents, Lloyd et al.[29] observed two one-electron steps. The first process was reversible and the second irreversible. The potential separating the two processes was approximately 1 V. In our work, the difference in potential between the two oxidation processes is about 0.5 V. However, generally results for the hormonal steroids parallel those of electrochemical studies of related arene complexes in dichloromethane.

In other reports,[26,27,33–37] coordinating solvents such as acetonitrile and dimethylformamide have been used. Frequently, irreversible waves were observed in such media and the total number of electrons associated with the oxidation process seems to vary between two and three. In the presence of coordinating ligands, alternative pathways are available for releasing the electronic strain. E.g., formation of a 19-electron intermediate by direct addition of a ligand[25] or formation of a metal carbonyl complex with loss of arene.[33–37] These solvent-assisted pathways are not available in a noncoordinating solvent, such as dichloromethane, and cannot be considered in the present work. However, clearly the mechanism proposed is a form of a 19-electron intermediate achieved via an internal rearrangement and in this sense bears some resemblance to the mechanism proposed by Doxsee, Grubbs, and Anson[25] to explain reactivity in the presence of coordinating ligands.

Acknowledgment. Valuable discussions with Ray Colton and Dwight Sweigart throughout the course of this work are gratefully acknowledged as is financial assistance to C.B.P. and Deakin University provided by the International Development Program of Australian Universities and Colleges.

Registry No. Estradiol, 50-28-2; estrone, 53-16-7; estrone 3-methyl ether, 1624-62-0; $Cr(CO)_3$ (estradiol), 77109-92-3; $Cr(CO)_3$ (estrone 3-methyl ether), 12171-88-9; $Cr(CO)_3$ (estrone), 12243-26-4; $Mo(CO)_3$ (estradiol), 77089-95-3; $W(CO)_3$ (estradiol), 77089-96-4.

Photochemical Reaction of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ with 1,3-Butadiene in Liquid Xenon Solution: Possible Intermediates in the Catalytic Dimerization of Dienes

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IR spectroscopic evidence is presented showing that UV photolysis of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ in liquid Xe (LXe) doped with 1,3-butadiene (C_4H_6) yields η^2-C_4H_6 and η^4-C_4H_6 complexes of Co (**1** and **2**) and Fe (**3–5**). Under similar photolytic conditions in liquid Kr, $Ni(CO)_4$ forms only $Ni(CO)_3(\eta^2\text{-}C_4H_6)$, which is thermally less stable than the compounds of Fe and Co. Both $Co(CO)_2(NO)(\eta^2\text{-}C_4H_6)$ (**1**) and $Fe(CO)(NO)_2(\eta^2\text{-}C_4H_6)$ (**3**) are thermally stable up to −35 °C in LXe. $Co(CO)(NO)(\eta^4\text{-}C_4H_6)$ (**2**) reacts thermally with CO to regenerate **1** with an enthalpy of activation $6 < \Delta H^{*} < 15$ kcal mol^{-1} and a half-life of ~11 min at −41 °C. $Fe(NO)_2(\eta^4\text{-}C_4H_6)$ (**5**) has a similar thermal stability. Only $Fe(CO)_2(NO)_2$, a known catalyst for photodimerization of butadiene, forms a bis(butadiene) complex, $Fe(NO)_2(\eta^2\text{-}C_4H_6)_2$ (**4**), which is a likely candidate for the catalytically active intermediate. We suggest that catalysis may proceed via a five-coordinate intermediate $Fe(NO)_2(\eta^2\text{-}C_4H_6)(\eta^4\text{-}C_4H_6)$ (**8**) with a bent NO group. Species **1** through **5** have been characterized by observation of IR bands due not only to ν(CO) and ν(NO) but also to coordinated C_4H_6. Tentative assignments of these C_4H_6 spectra are given.

Introduction

It has been known for many years that transition-metal nitrosyl compounds can photocatalyze the dimerization of dienes.[1–3] Particularly striking is the contrast between $Fe(CO)_2(NO)_2$, a highly specific catalyst for the dimerization of butadiene to 4-vinylcyclohexene,[2] and $Co(CO)_3NO$, which is catalytically almost inactive.[2] A number of detailed studies have together shown that "$Fe(NO)_2$" is the active catalyst. Carbon monoxide suppresses catalysis[1,2] while "$Fe(NO)_2$" precursors such as $[Fe(NO)_2Cl]_2$ can be used to generate catalysts.[4] Furthermore, Fe-

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$(NO)_2(PPh_3)_2$ is not a catalyst[1] presumably because it does not easily lose its PPh_3 ligands to form "$Fe(NO)_2$".

By contrast, relatively little is known about the interaction of "$Fe(NO)_2$" and the diene substrates. Jolly et al. suggested[1] that, for norbornadiene, dimerization occurred "intramolecularly in a sterically critical tetrahedral complex". They also made the perceptive suggestion that the specificity of the dimerization was an indication that the second, formally uncoordinated, π bonds of the dienes were involved in the transition state. However, apart from a transient ν(NO) IR absorption[1] at 1745 cm^{-1}, no intermediates have been observed. In this paper we show that liquid xenon can be used to characterize several nitrosyl complexes of both Fe and Co, which are possible intermediates in the dimerization of 1,3-butadiene.

Although liquid xenon (LXe) and liquid krypton (LKr) are somewhat unconventional solvents, they have already proved most successful for characterizing unstable organometallic species, particularly those containing coordinated N_2,[5,6] molecular H_2,[7,8] or alkenes.[9,10] The success of these solvents is primarily due to a combination of low temperatures, which reduce rates of thermal decomposition, and the complete absence of IR absorptions throughout the mid-IR. Under these conditions FT-IR spectroscopy becomes a very sensitive and diagnostic technique for detecting coordinated organic ligands.[9,10]

We have already reported a number of photochemical reactions[6,7,9] of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ in LXe and LKr. These experiments showed a significant difference between Co and Fe. $Co(CO)_3NO$ yielded only monosubstituted products $Co(CO)_2(NO)L$ (L = N_2 or 1-butene) under conditions where $Fe(CO)_2(NO)_2$ gave both mono- and disubstituted products.

In this paper, we show that reactions of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ with 1,3-butadiene are somewhat more complicated because both η^2-C_4H_6 and η^4-C_4H_6 complexes are formed. Most surprisingly the η^4 complexes are thermally more reactive than η^2. In what follows, we first present the spectroscopic evidence for the formation of these different complexes and then discuss briefly their relevance to the catalytic dimerization of dienes.

Experimental Section

The detailed design of the low-temperature cell and its specific application to organometallic photochemistry have been described previously.[5,7,11] The cell used in these experiments had an optical path length of 2.7 cm and a maximum operating pressure of 20 atm (corresponding to the vapor pressure of LXe at −30 °C). The solution was magnetically stirred.

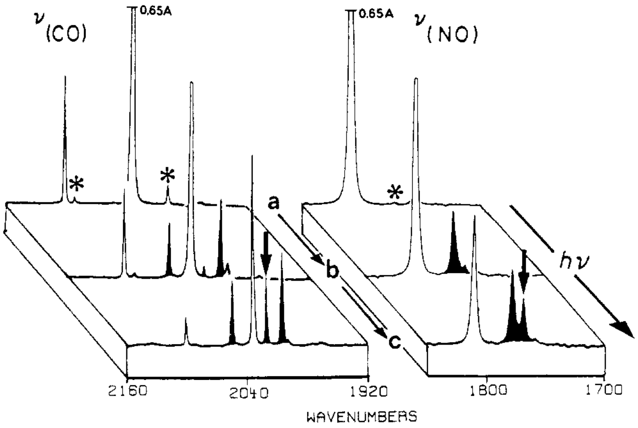

Figure 1. IR spectra showing the photolysis of $Co(CO)_3NO$ in LXe doped with C_4H_6 ($\sim10^{-4}$ M) at −104 °C: (a) before UV photolysis (bands are due to $Co(CO)_3NO$; those marked with asterisks are ^{13}CO, ^{18}O, and ^{15}N satellites in natural abundance); (b) after 55-s UV photolysis (the bands colored black are due to the primary photoproduct **1**); (c) after 190-s UV photolysis (the two arrowed bands are due to the secondary photoproduct **2**).

IR spectra were obtained with a Nicolet MX-3600 FT-IR interferometer and 1180E data system. Interferograms were collected with 16K or 32K data points (2 or 0.7 cm^{-1} resolution) and were transformed with Box-car Apodization by using 32K or 256K transform points. Particularly relevant to this paper is the detailed description[9,12] of the IR spectral subtraction procedures required to unravel the relatively weak absorptions due to coordinated organic ligands from the absorptions due to unreacted ligand and metal nitrosyl.

In any experiment where structural information is to be extracted from weak IR bands, it is vital to prove that these bands are due to the same molecule as the intense ν(CO) and ν(NO) bands. This proof requires that the weak and intense bands maintain constant relative intensities as the concentration of the molecule varies during the experiment. Although the disparity in intensities of the bands prevents a direct quantitative comparison, we have already shown[9] that relative band intensities can be conveniently monitored by using the relatively weaker 2ν(CO) and 2ν(NO) overtone bands and isotopic satellites. Such measurements have been made on all of the compounds reported here.

$Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ were prepared by standard procedures.[13] $Ni(CO)_4$ was degassed under liquid nitrogen prior to use. Xe, Kr (BOC research grade), and butadiene (Matheson) were used without further purification.

All photolysis was carried out with a 250-W high-pressure Hg arc (λ < 280 nm).

Results

Photolysis of $Co(CO)_3NO$ and Butadiene in LXe. Figure 1 shows the IR spectra obtained when $Co(CO)_3NO$ was photolyzed in LXe in the presence of C_4H_6. After brief UV photolysis, two new ν(CO) bands and one ν(NO) band appeared (colored black in Figure 1b). On further photolysis we observed two additional bands (one ν(CO) and one ν(NO), arrowed in Figure 1c), assignable to a second photoproduct. UV photolysis also generated a weak IR band due to uncoordinated CO, dissolved in LXe (not illustrated). These spectra are consistent with a primary photoproduct, **1**, containing the $Co(CO)_2NO$ moiety, and a secondary photoproduct, **2**, containing Co(CO)NO.

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Table I. Wavenumbers (cm^{-1}) of the Principal IR Bands of $Co(CO)_2(NO)(\eta^2\text{-}C_4H_6)$ (1) and $Co(CO)_2(NO)(\eta^2\text{-1-butene})$ in LXe at -104 °C

η^2-C_4H_6 (1)		η^2-1-butene[b]		assignment
2056.0	2057.6 (sh)[a]	2053.6		ν(CO) a′
2005	2007 (sh)[a]	2000.1		ν(CO) a″
1778.9		1776.6		ν(NO) a′
1513		1534.0		ν(C=C)
2046.3	2041.2	2040	2038.0	ν(CO) } (^{13}CO)–(^{12}CO)[c,d]
1978.0	1973.3	1970.4	1968.1	ν(CO)
1743.2		1740.6		ν(CO) (^{15}NO)/(N^{18}O)
4103		4097.4		2 × a′(CO)
4034		4028.4		a′(CO) + a″(CO)
3997		3985.3		2 × a″(CO)
3531		3527.1		2 × a′(NO)

[a] Shoulders are assigned to different conformers of the organic ligand.[9,14] [b] Taken from ref 9 which also contains data on $Co(CO)_3NO$ under the same conditions. [c] Using ^{13}CO-enriched $Co(CO)_3NO$, additional bands of 1 were observed at 2010.3, 1961.8 (sh), and 1960.2 cm^{-1} due to $Co(^{13}CO)_2(NO)(\eta^2\text{-}C_4H_6)$. [d] ^{13}CO data were successfully fitted by using the following C–O factored force constants; 1 first isomer, k_{CO} = 1665.83 and $k_{CO,CO}$ = 41.71 Nm^{-1}; 1, second isomer, k_{CO} = 1668.68, $k_{CO,CO}$ = 41.45, and k_{NO} = 1392.0 Nm^{-1}; $Co(CO)_2(NO)$(1-butene),[9] k_{CO} = 1662.1, k'_{CO} = 1657.20, $k_{CO,CO}$ = 43.735, and k_{NO} = 1388.48 Nm^{-1}.

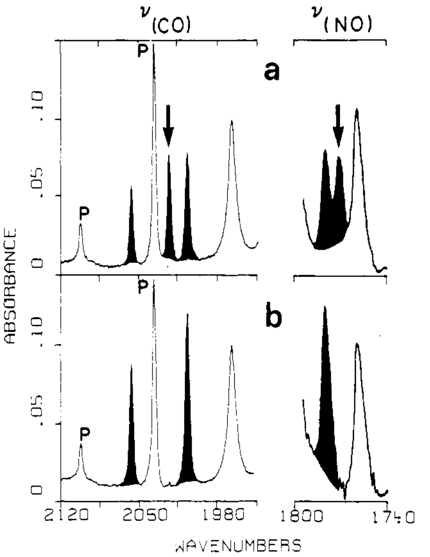

Figure 2. IR spectra showing the thermal reaction of 2 to reform 1 in LXe at −41 °C: (a) spectrum after UV photolysis (the bands marked P are due to unphotolyzed $Co(CO)_3NO$, black bands are due to 1, *arrowed* bands are due to 2, and unlabeled bands are due to free C_4H_6 in the solution (note the concentration of C_4H_6 is much higher than in Figure 1)); (b) spectrum after 41-min thermal decay (the arrowed bands due to 2 have disappeared, and the black bands due to 1 have increased substantially in intensity). Note that the ν(NO) region of the spectrum is plotted with ×1$^1/_2$ expansion in absorbance relative to the ν(CO) region.

Neither photoproduct was observed in the absence of butadiene. Thus the overall photochemistry can be summarized by eq 1, where X and Y are ligands derived from butadiene.

$$Co(CO)_3NO \xrightarrow[-CO]{UV} \underset{1}{Co(CO)_2(NO)X} \xrightarrow[-CO]{UV} \underset{2}{Co(CO)(NO)Y} \qquad (1)$$

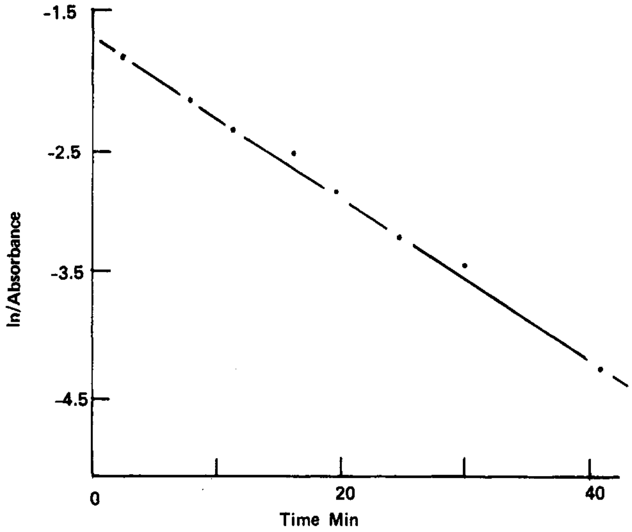

Figure 3. Plot of ln [absorbance] of the ν(NO) band of 2 (arrowed in Figures 1 and 2) vs. time illustrating the pseudo-first-order reaction of 2 with CO at −41 °C in LXe.

Table II. Wavenumbers (cm^{-1}) of ν(CO) and ν(NO) Bands of $Co(CO)(NO)(\eta^4\text{-}C_4H_6)$ (2) in LXe at -104 °C

obsd	calcd[b,c]	assignt
2021.7		a′ ν(CO)
1976.1	1976.64	a′ ν(^{13}CO)
1769.6		a′ ν(NO)
1734?[a]	1738/1723	a′ ν(^{15}NO)/a′ ν(N^{18}O)

[a] Very weak. [b] Calculated from ν(^{12}CO) and ν(^{14}NO) using the appropriate reduced masses. Note agreement for ^{15}NO and N^{18}O is usually poor in such calculations.[6,9] [c] Force constants k_{CO} = 1651.0 and k_{NO} = 1377.52 Nm^{-1}.

The ν(CO) and ν(NO) bands of 1 are very close in frequency to those of $Co(CO)_2(NO)(\eta^2\text{-1-butene})$[9] (Table I). The agreement extends even to isotopic satellites, overtone and combination bands, which establish the presence of the $Co(CO)_2NO$ moiety. This suggests that 1 is $Co(CO)_2(NO)(\eta^2\text{-}C_4H_6)$, an assignment which is confirmed by the IR bands of the coordinated C_4H_6 (see below). The ν(CO) bands of 1 have partially resolved shoulders[14] which are similar to those observed for the butene complex, where they were shown to result from different conformers of the coordinated butene.[9]

2 is thermally unstable and reacts with CO to reform 1 as illustrated in Figure 2. In the presence of excess CO and C_4H_6, this reaction follows good first-order kinetics over at least three half-lives; see Figure 3. The rate of the reaction was unaffected by a 65-fold increase in concentration of C_4H_6 in the LXe solution. Thus, 2 is unlikely to be the bis(butadiene) complex $Co(CO)(NO)(\eta^2\text{-}C_4H_6)_2$ since by analogy with the Fe system (see below) the reaction rate of this compound would be expected to depend on the concentration of C_4H_6.

Over the temperature range 205–232 K, the decay of 2 → 1 has an apparent enthalpy of activation, $\Delta H^{\ddagger}$, of 6 kcal mol^{-1}. Kinetic measurements[5] were not made with a deliberate variation in the concentration of CO, but the

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(14) For both 1 and 3 the splittings of the ν(CO) bands changed reversibly on warming from −104 to −41 °C. In the case of 1 the shoulder merged into the broadened band on warming, while for 3 the weaker low wavenumber band increased in intensity relative to the high wavenumber band. The behavior in 3 was consistent with two isomers of almost equal energy, ΔH = 0.3 kcal mol^{-1}. A possible assignment of these isomers would involve *cis*- and *trans*-η^2-C_4H_6 but the energy difference is rather low for such a large change in structure. Small splittings are also observed in the bands of η^2-C_4H_6; see Table VI. The presence of two isomers makes the analysis of the ^{13}C–O satellites rather more complicated than would have been expected for structures 1 and 3; see Tables I and IV.

(15) UV photolysis of an *unstirred* LXe solution containing relatively high concentrations of $Fe(CO)_2(NO)_2$ yield a product with three strong IR bands 1885, 1787, and 1761 cm^{-1} and a number of weak bands (1600–1100 cm^{-1}) due to a coordinated organic ligand, not obviously either η^2-or η^4-C_4H_6. As soon as the solution was stirred, all of these bands dropped dramatically in intensity and a reddish precipitate was formed. Since the bands were only observed with high concentrations of $Fe(CO)_2(NO)_2$, they may well be due to a polynuclear product.

Table III. Kinetic Data for the Pseudo-First-Order Reaction of $Co(CO)(NO)(\eta^4\text{-}C_4H_6)$ (2) with CO in LXe Solution

temp, °C	$10^4\ k_{obsd}$,[a] s^{-1}	$10^3\ A_{CO}$[b]	rel [CO][c,d]
−68	1.1	4.7	1
−62	2.2	2.63	0.56
−50	5.9	1.2	0.25
−41	10.1	0.5	0.11

[a] Observed pseudo-first-order rate constant. An Eyring plot (ln $[k_{obsd}/T]$ against $1/T$) gives $\Delta H^\ddagger \approx 6$ kcal mol^{-1}. [b] Peak absorbance of the IR band due to dissolved CO in the solution. [c] Relative concentrations of free CO in solution, assuming that the concentration is proportional to the peak absorbance (i.e., that there is no change in half-width of the band with temperature). Unfortunately we cannot easily translate these relative concentrations into absolute concentrations because the extinction coefficient of CO under these conditions is not known. The concentrations of **2** and C_4H_6 were $\sim 10^{-6}$ and $\sim 2 \times 10^{-3}$ M, respectively. [d] An Eyring plot of ln $(k_{obsd}/[CO]T)$ against $1/T$ gives $\Delta H^\ddagger \approx 15$ kcal mol^{-1}. In the absence of an absolute value of [CO] $\Delta S^\ddagger$ cannot be evaluated.

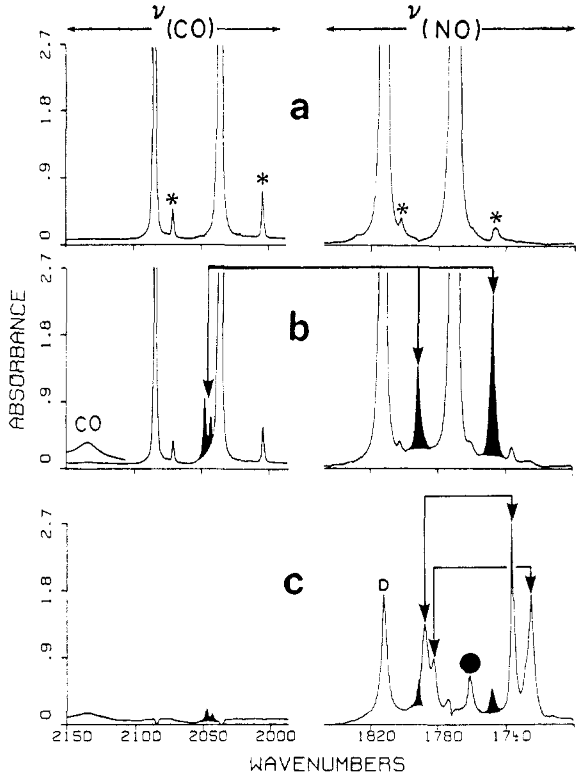


Figure 4. IR spectra illustrating UV photolysis of $Fe(CO)_2(NO)_2$ in LXe doped with C_4H_6 at −104 °C: (a) before photolysis (bands are due to $Fe(CO)_2(NO)_2$, and asterisks mark natural abundance isotopic satellites); (b) after brief UV photolysis (bands due to **3** are arrowed; note the band of free CO shown with ×20 absorbance expansion); (c) after prolonged UV photolysis, when all of the $Fe(CO)_2(NO)_2$ has been destroyed (the arrowed bands are due to **4** and **5**, the band marked D is due to free C_4H_6, and the band marked ● is due to a further product, possibly polynuclear).[15]

concentration of dissolved CO drops as the solution is warmed. Allowing for this variation in concentration of CO, we obtain $\Delta H^\ddagger = 15$ kcal mol^{-1}. The true value of $\Delta H^\ddagger$ presumably lies between 6 and 15 kcal mol^{-1}. The spectroscopic data for **2** are summarized in Table II and the kinetic data in Table III.

The observed behavior of **2** (eq 2) is therefore consistent with the complex $Co(CO)(NO)(\eta^4\text{-}C_4H_6)$, and below we use the IR spectrum of coordinated butadiene to confirm this assignment.

$$\underset{\mathbf{1}}{Co(CO)_2(NO)(\eta^2\text{-}C_4H_6)} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \mathbf{2} + CO \qquad (2)$$

Table IV. Wavenumbers (cm^{-1}) of the Principal IR Bands of $Fe(CO)(NO)_2(\eta^2\text{-}C_4H_6)$ (3) and $Fe(CO)(NO)_2(\eta^2\text{-1-butene})$ in LXe at −104 °C

$(\eta^2\text{-}C_4H_6)$ (3)	$(\eta^2$-1-butene)[c]	assignt[d]
2047.6/2043.3[a]	2042.3/2035.3[a]	ν(CO) a′
1791.6	1789.7	ν(NO) a′
1748.5	1745.8	ν(NO) a″
1506	1525	ν(C=C)
2002.0/1998.1[a]	1997.1/1990.5[a]	ν(CO) (^{13}CO)
b	*b*	ν(NO) (^{15}NO)(NO),
1723.5	1721.5	ν(NO) (NO)(N^{18}O)
b	4056.2/4043.7	2 × a′ (CO)
3572.6	3567	2 × a′(NO)
3514.8	3509.7	a′(NO) + a″(NO)
3482.8	3476	2 × a″(NO)

[a] Splittings assigned to different rotamers of the coordinated organic ligand.[9,14] [b] Not observed, overlapped by absorptions of other species. [c] Taken from ref 9 which also contains data on $Fe(CO)_2(NO)_2$ under these conditions. [d] Isotopic satellites were successfully fitted by using the energy factored force constants: **3**, k_{CO} = 1693.53, k_{CO} (second isomer) = 1686.41, k_{NO} (both isomers) = 1378.40, and $k_{NO,NO}$ = 33.53 Nm^{-1}; $Fe(CO)(NO)_2$(1-butene),[9] k_{CO} = 1684.8/1673.3, k_{NO} = 1374.8, and $k_{NO,NO}$ = 34.14 Nm^{-1}.

Table V. Wavenumbers (cm^{-1}) of ν(NO) Bands and Overtones (Where Observed) of $Fe(NO)_2(\eta^2\text{-}C_4H_6)_2$ (4), $Fe(NO)_2(\eta^2\text{-1-butene})$, and $Fe(NO)_2(\eta^4\text{-}C_4H_6)$ (5) in LXe at −104 °C

$(\eta^2\text{-}C_4H_6)_2$ (4)	$(\eta^2$-1-butene$)_2$[a]	$(\eta^4\text{-}C_4H_6)$ (5)	assignt
1776.5	1766.4	1787.5	a′ ν(NO)
1726	1720.3	1736.3	a″ ν(NO)
		3457.8	2 × a″
	3486.7	3493	a′ + a″

[a] From reference 9.

Photolysis of $Fe(CO)_2(NO)_2$ and Butadiene. The spectra illustrated in Figure 4 show the results of UV photolysis of $Fe(CO)_2(NO)_2$ and C_4H_6 in LXe. The primary photoproduct **3** has one ν(CO) and two ν(NO) absorptions (Figure 4b), and free CO is formed at the same time (eq 3).

$$Fe(CO)_2(NO)_2 \xrightarrow[C_4H_6]{UV} \mathbf{3} + CO \qquad (3)$$

After prolonged UV photolysis two further photoproducts, **4** and **5**, are observed, both with two ν(NO) bands and neither with any ν(CO) absorptions (Figure 4c). Both **4** and **5** are thermally unstable and decay when the solution is warmed to −50 °C. **4** decays more slowly if the concentration of C_4H_6 in solution is increased, while the decay rate of **5** is unaffected.

The ν(CO) and ν(NO) bands of **3** (including isotopic satellites and overtones) are extremely close in frequency to those of $Fe(CO)(NO)_2(\eta^2\text{-1-butene})$[9] (Table IV), and as with the butene complex the ν(CO) band of **3** was found to be split into a doublet.[14] In the butene complex this doublet was shown[9] to be due to cis and gauche conformers of coordinated butene.

The ν(NO) frequencies of **4** are quite close to those of $Fe(NO)_2(\text{1-butene})_2$[9] while those of **5** are not (Table V). We now look at the IR bands associated with the coordinated butadiene and show that **3** and **4** contain $\eta^2\text{-}C_4H_6$ and that **5** contains $\eta^4\text{-}C_4H_6$.

IR Bands of Coordinated Butadiene. Figure 5 shows the IR bands associated with coordinated C_4H_6 in the primary photoproducts of photolysis of $Fe(CO)_2(NO)_2$ (trace a) and $Co(CO)_3NO$ (trace b). The two spectra are almost identical. Both have characteristic bands ~1510 cm^{-1} (arrowed) assignable to ν(C=C) vibrations of coordinated olefins.[16] Both spectra also show bands ~1620

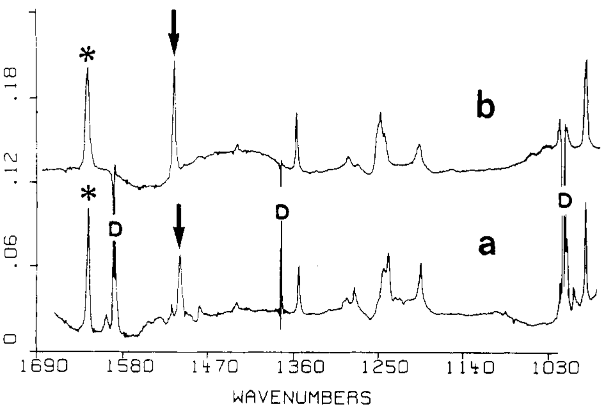
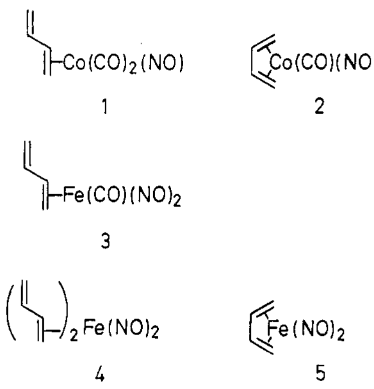


Figure 5. IR bands associated with coordinated butadiene in (a) $Fe(CO)(NO)_2(\eta^2-C_4H_6)$ (**3**) and (b) $Co(CO)_2(NO)(\eta^2-C_4H_6)$ (**1**) in LXe solution at -104 °C. The arrows mark the bands assigned to ν(C=C) vibrations of the *coordinated* C=C double bonds and the asterisks the ν(C=C) bands of *uncoordinated* C=C bonds.[15] The bands marked D are residual absorptions of free C_4H_6, left after computer subtraction. Tentative assignments of these spectra are given in Table VI.

Chart I



cm^{-1}, marked with asterisks, due to the ν(C=C) vibration of the uncoordinated C=C bond in η^2-C_4H_6. These spectra correspond closely to the reported IR spectrum[18] of $Fe(CO)_4(\eta^2-C_4H_6)$, and tentative assignments of the complete spectra are given in Table VI. Even without these detailed assignments, the spectra confirm our identification of the primary photoproducts as the η^2-complexes **1** and **3** (see Chart I).

The identification of the secondary photolysis products is also relatively straightforward. The IR spectra associated with coordinated C_4H_6 in these photoproducts are shown in Figure 6. Spectrum 6b is due to **2** the secondary product from $Co(CO)_3NO$. It is clear that this spectrum has no band above 1580 cm^{-1} which could be assigned to the uncoordinated C=C bond of an η^2-C_4H_6 ligand. The spectrum does, however, bear a close resemblance to that of $Fe(CO)_3(\eta^4-C_4H_6)$[19] (Figure 6c) particularly in the pattern of three strong bands in the region 1250–1030 cm^{-1} (indicated by a brace). Thus the spectra confirm that **2** is $Co(CO)(NO)(\eta^4-C_4H_6)$.

Table VI. Tentative Assignment and Wavenumbers (cm^{-1}) of Principal Bands of η^2-C_4H_6 in $Co(CO)_2(NO)(\eta^2-C_4H_6)$ (1), $Fe(CO)(NO)_2(\eta^2-C_4H_6)$ (3), and $Fe(CO)_4(\eta^2-C_4H_6)$

$Co(CO)_2NO^a$ (1)	$Fe(CO)(NO)_2{}^{a,b}$ (3)	$Fe(CO)_4{}^c$	assignt^e
1624.5 s/26 sh^f	1624 s	1620 s	[ν(C=C)]
1513 m	1506 m	1487 m	ν(C=C)
1355 m	1353	1340 vw	δ(=CH_2) scissors
1288 w	1290 w	1289 w	[δ(=CH) bend]
1274 w			
1245.3/40 m^f	1241 m/35.5 sh^f		ν(C—C)
1195 w	1193 m	1202 s	δ(=CH) bend
1011 m/1005 sh^f	1006 m	1015 w	[δ(=CH) wag]
982 sh/980.3 s^f	981 s	980 m	[δ(=CH_2) rock]
949.8 w	943 w	920 w^d	δ(=CH) wag
903 s/900.6 s^f	901.6	888 s^d	[δ(=CH_2) wag]
775 m/769 sh^f	774 m/770 sh^f		δ(=CH_2) wag

[a] This work. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; vs, very strong. [b] The bands of $Fe(NO)_2(\eta^2-C_4H_6)_2$ are extremely close in frequency to those of **3** and, apart from [ν(C=C)] at 1618 cm^{-1}, have not been tabulated separately. [c] Reference 18 tetrachloroethylene solution. [d] Reference 18, SO_2 solution. [e] The bands are assigned on the basis of coordinated and uncoordinated olefinic groups.[16] The uncoordinated group assignment is indicated by square brackets. [f] Splittings due to different rotamers.[14]

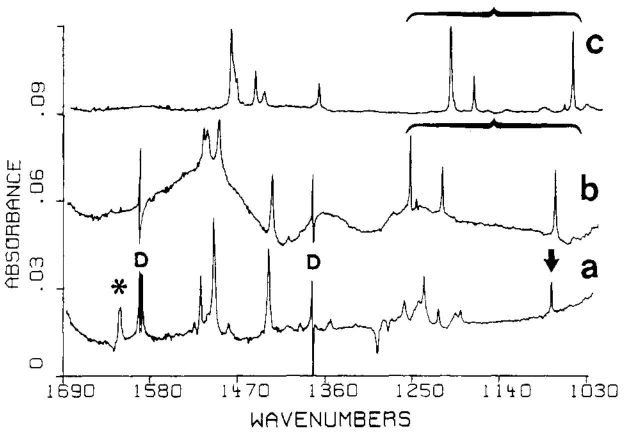


Figure 6. IR bands associated with coordinated butadiene in the secondary photoproducts in LXe at -104 °C: (a) spectrum of a mixture of **4**, $Fe(NO)_2(\eta^2-C_4H_6)_2$, and **5**, $Fe(NO)_2(\eta^4-C_4H_6)$ (the asterisk marks the ν(C=C) of the *uncoordinated* C=C bond in **4**, and the arrow shows one band due to η^4-C_4H_6 in **5**; note that this sample contained very little **3**, $Fe(CO)(NO)_2(\eta^2-C_4H_6)$; cf. Figure 4c); (b) spectrum of **2**, $Co(CO)(NO)(\eta^4-C_4H_6)$ (D marks residual absorptions of free C_4H_6; the broad humps in the spectrum are artefacts due to computer subtraction); (c) spectrum of an authentic sample of $Fe(CO)_3(\eta^4-C_4H_6)$—Strem Chemicals Inc.—dissolved in LXe. Note the similar pattern of the bands marked by braces in (b) and (c).

Figure 6a shows the spectrum of an LXe solution containing a mixture of the two secondary photoproducts **4** and **5**, derived from $Fe(CO)_2(NO)_2$. These have already been tentatively identified as $Fe(NO)_2(\eta^2-C_4H_6)_2$ (**4**) and $Fe(NO)_2(\eta^4-C_4H_6)$ (**5**). Even without a detailed analysis of the spectrum one can pick out features associated both with η^2- and with η^4-C_4H_6 ligands. These features are a band at 1618 cm^{-1} marked with an asterisk, attributable to the ν(C=C) vibration of an uncoordinated olefinic bond

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(16) In olefins and dienes, the various normal modes are considerably mixed but it is generally agreed that vibrations in the region of 1600 cm^{-1} are largely ν(C=C) in character.[9] In 1,3-butadiene the situation is further complicated because the ν(C=C) modes of the two conjugated C=C bonds are coupled.[17] This coupling gives rise to a strong IR band (b_u under the C_{2h} point group) at 1591 cm^{-1} and a formally IR-forbidden mode[16] (a_g symmetry) which is nevertheless observed as a very weak IR band at 1653 cm^{-1} in LXe at -104 °C. If the two C=C vibrators could be uncoupled, one would expect them both to absorb at 1622 cm^{-1}, i.e., (1653 + 1591)/2. η^2-Coordination of C_4H_6 will effectively uncouple the ν(C=C) modes. In this case, one would expect the band due to the uncoordinated C=C bond to be unshifted at ~1622 cm^{-1} while, by analogy with 1-butene complexes, the band of the coordinated C=C bond should be lowered in frequency to ~1520 cm^{-1}. Our tentative assignment of the bands of η^2-C_4H_6 uses this "coordinated/uncoordinated" formalism for all the bands in the range 1650–750 cm^{-1} (Table VI).

(17) Panchenko, Y. N.; Pulay, P.; Torok, F. *J. Mol. Struct.* **1976**, *34*, 283.

(18) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1962**, *45*, 1157.

(19) Gadd, G. E.; Davidson, G.; Davies, C. L., to be submitted for publication.

Table VII. Tentative Assignment and Wavenumbers (cm^{-1}) of Principal Bands Associated with η^4-C_4H_6 in $Co(CO)(NO)(\eta^4$-$C_4H_6)$ (2), $Fe(NO)_2(\eta^4$-$C_4H_6)$ (5), and $Fe(CO)_3(\eta^4$-$C_4H_6)$ in LXe at −104 °C

Co(CO)(NO) (2)	$Fe(NO)_2$ (5)	$Fe(CO)_3$[a,b]	assignt[a]
1513	1516	1476/79 (1476 dp, 1482.5 pol, sh)	a″ ν(C=C)
1509			a′
1494	1499.4	1448 (1450 pol)	a′ δ(=CH_2) scissors
1426	1430	1368 (1372.5 pol)	a″
1252	1235.5	1201	a′ δ(=CH) bend
1211	1189	1171 (1175 dp)	a″
910	~918	925 (927 pol)	a′ ν(C—C)
934	962.5	951 (952 pol)	a′ δ(=CH) wag
1069.5	1075	1047 (1050.5 dp)	a″
881	894	893 (896 dp)	a″ δ(=CH_2) wag

[a] Taken from ref 12 and 19. [b] Figures in parentheses are Raman bands also recorded in LXe at −104 °C; pol = polarized, dp = depolarized.

of η^2-C_4H_6 and an arrowed band in the region 1140–1030 cm^{-1}, a region where η^4-C_4H_6 is known to absorb (cf. Figure 6c) but where η^2-C_4H_6 has no bands (cf. Figure 5). Thus, the spectrum of 4 is consistent with $Fe(NO)_2(\eta^2$-$C_4H_6)_2$, and the spectrum of 5 suggests that it is $Fe(NO)_2(\eta^4$-$C_4H_6)$. Wavenumber data and tentative assignments are given in Table VII.

Comparison with $Ni(CO)_3(\eta^2$-$C_4H_6)$. The η^2-C_4H_6 complexes of Co and Fe, **1** and **3**, are formally isoelectronic with $Ni(CO)_3(\eta^2$-$C_4H_6)$ (**6**). How does the behavior of these compounds compare?

In a previously unpublished report,[11] Simpson observed three ν(CO) bands 2091, 2025, and 2022 cm^{-1} [and $\nu(^{13}CO)$ 1984 cm^{-1}] when $Ni(CO)_4$ was photolyzed in LKr doped with C_4H_6.[20] These bands were asigned to $Ni(CO)_3(\eta^2$-$C_4H_6)$ (**6**) with local C_s symmetry (2a′ + a″). The compound was thermally stable at 120 K even in the presence of added CO, but at 160 K it reacted with a half-lfe of only 70 s in presence of CO (4×10^{-3} M). Thus **6** is thermally much less stable than either **1** or **3**.

Even at low temperatures, there was no evidence for the formation of $Ni(CO)_2(\eta^4$-$C_4H_6)$. This again contrasts with the Co and Fe systems, where in both cases we observed the photochemical formation of η^4-C_4H_6 complexes **2** and **5**.

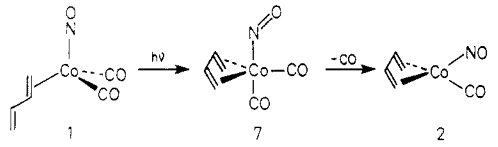
Discussion

Formation of η^4-C_4H_6 Complexes. The photosubstitution of CO by butadiene in metal carbonyls is well-known.[21,22] Such photosubstitution usually proceeds via an η^2-C_4H_6 complex to the η^4-complex by a dissociative pathway. A well-documented example[21,23] is $Fe(CO)_3(\eta^4$-$C_4H_6)$ which is formed from $Fe(CO)_5$ via $Fe(CO)_4(\eta^2$-$C_4H_6)$ and the 16-electron species $Fe(CO)_3(\eta^2$-$C_4H_6)$. It is characteristic of these substitutions that a bis(olefin) complex is formed when the unsubstituted carbonyl compound is photolyzed in the presence of a mono-olefin under conditions similar to those used for dienes[21] (eq 4 and 5).

$$Fe(CO)_5 \xrightarrow[\text{diene}]{h\nu} Fe(CO)_3(\eta^4\text{-diene}) \quad (4)$$

$$Fe(CO)_5 \xrightarrow[\text{olefin}]{h\nu} Fe(CO)_3(\eta^2\text{-olefin})_2 \quad (5)$$

Thus, it is not unexpected that $Fe(NO)_2(\eta^4$-$C_4H_6)_2$ (**5**) can be formed from $Fe(CO)_2(NO)_2$ since we have already shown that $Fe(NO)_2$(1-butene$)_2$ can be generated under similar conditions.[9] By contrast it is very surprising that $Co(CO)(NO)(\eta^4$-$C_4H_6)$ (**2**) can be formed photochemically from $Co(CO)_3(NO)$ in LXe solution since Co(CO)(NO)(1-butene$)_2$ cannot be generated by this route.[9,29] There is already evidence that $Co(CO)_3NO$ can undergo *associative* photochemical substitution reaction[24] and we suggest that **1** may perhaps be converted to **2** by an associative mechanism, involving the 18-electron intermediate **7** (eq 6).



(6)

Once formed the η^4-C_4H_6 complexes **2** and **5** are thermally more reactive toward CO than the corresponding η^2-C_4H_6 complexes **1** and **3**. This is the opposite of what is normally observed; η^4-diene compounds are generally less reactive than η^2-diene complexes.[23] Unfortunately, more detailed kinetic information will be required before we can understand in detail why **2** and **5** are so reactive toward CO. However, in the present context it is more significant that **2** and **5** do not appear to react with butadiene, either photochemically or thermally, under the conditions of our experiment.

A Possible Mechanisms for Catalytic Dimerization. $Fe(NO)_2(\eta^2$-$C_4H_6)_2$ (**4**) seems to be a strong candidate for the active intermediate in dimerization.[25] The fact that Fe forms a bis(butadiene) complex, **4**, while Co does not form $Co(CO)(NO)(\eta^2$-$C_4H_6)_2$ provides a straightforward rationalization of why $Co(CO)_3NO$ is a poor dimerization catalyst.[2]

The relative concentrations of $Fe(CO)_2(NO)_2$ and butadiene in our experiments (usually 1:500–1:5000) were comparable to those used by previous workers for catalytic studies.[1,2] In our experiments, however, both the temperature and the absolute concentration of butadiene, ~ 10^{-3} M, were very much lower than were used previously so that it is not surprising that we did not observe catalytic dimerization. The effect of higher concentrations of diene would be to increase greatly the lifetime of **4** relative to the η^4-diene complex **5**.

In the absence of other observed intermediates, any proposal about how **4** leads to catalytic dimerization is necessarily speculative. However, following our suggestion that η^4-C_4H_6 complexes could be formed by an associative

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(20) UV photolysis with a 125-W medium-pressure Hg arc or a Cd lamp (229 nm)[5]. IR spectra ere recorded with a Perkin-Elmer Model 283B spectrometer.

(21) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

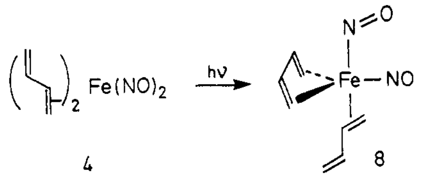
(22) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 1264.

(23) Ellerhorst, G.; Gerhartz, W.; Grevels, F.-W. *Inorg. Chem.* **1980**, *19*, 67.

(24) Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635. Zink, J. I., personal communication.

(25) For stable compounds, ν(CO) and ν(NO) IR bands in LXe are at similar wavenumbers to those in hydrocarbon solution at room temperature. Thus by comparison with **3**, we suggest that the transient ν(NO) band observed by Jolly et al.[1] at 1745 cm^{-1} was probably due to $Fe(CO)(NO)_2(\eta^2$-Norbornadiene).

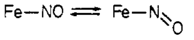
process, we propose $Fe(NO)_2(\eta^2\text{-}C_4H_6)(\eta^4\text{-}C_4H_6)$ (**8**) as a likely intermediate (eq 7).



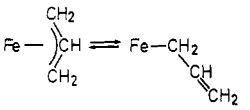
4 **8** (7)

This intermediate, **8**, is attractive because it provides a rationalization for several so-far unexplained features of the photocatalytic dimerization.[26] **8** contains three coordinated C=C bonds, and such an intermediate might lead specifically to the formation of 4-vinylcyclohexene rather than other possible dimers such as cyclooctadiene. Equally, it can be understood why "$Fe(NO)_2$" might be a less efficient catalyst for the dimerization of unconjugated dienes,[2] e.g., 1,5-hexadiene, because in this case formation of an η^4-diene intermediate would be sterically less favorable.

Formation of **8** involves one NO group changing from a three-electron to a one-electron donor (eq 8). A similar



(8)



(9)

change in electron donation can occur for the π-allyl ligand (eq 9), and it is interesting to note that "$Fe(NO)(\pi\text{-allyl})$" is as efficient as "$Fe(NO)_2$" in catalyzing dimerization of dienes.[2]

It is of course in the nature of catalytic intermediates that they are short-lived and not easily detected. However, **8** has a bent nitrosyl group and such groups have characteristic IR absorptions.[27] Thus, it is to be hoped that developments in fast-time-resolved IR spectroscopy[28] will allow us to detect **8** in the near future.

Conclusions

In this paper we have presented evidence for the formation of five new compounds during the photolysis of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ in the LXe doped with butadiene. Three of these compounds, **1**, **3**, and **4**, contain $\eta^2\text{-}C_4H_6$ and the other two, **2** and **5**, contain $\eta^4\text{-}C_4H_6$. It should be stressed that although the compounds have not been isolated as crystalline solids, the very detailed IR data combined with observations on thermal reactions provide strong evidence for the proposed structures.

Our most significant observations are that (i) $Co(CO)_3NO$ forms the $\eta^4\text{-}C_4H_6$ complex **2** under conditions where it does not normally yield disubstituted $Co(CO)(NO)(L)_2$ complexes, (ii) the $\eta^4\text{-}C_4H_6$ complexes of both Fe and Co are thermally *less* stable than the corresponding $\eta^2\text{-}C_4H_6$ compounds, and (iii) $Fe(CO)_2(NO)_2$ *does* form $Fe(NO)_2(\eta^2\text{-}C_4H_6)_2$ (**4**) a strong candidate for the catalytic intermediate.

The reactions of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ with butadiene are some of the most complicated which we have studied in LXe solution. Nevertheless, it is clear that IR techniques can successfully unravel problems of this complexity, and we are now extending our studies to the catalytic hydrogenation of dienes.

Acknowledgment. We thank the SERC and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. We thank Dr. D. Ballivet-Tkachenko for catalyzing our interest in these reactions. We thank Mr. J. G. Gamble, Dr. F.-W. Grevels, Dr. M. A. Healy, Dr. R. K. Upmacis, Dr. M. B. Simpson, and Dr. A. H. Wright for their help and advice.

Registry No. **1**, 105162-61-6; **2**, 105162-62-7; **3**, 105162-63-8; **4**, 105162-64-9; **5**, 105162-65-0; **8**, 105162-66-1; $Co(CO)_3NO$, 14096-82-3; $Fe(CO)_2(NO)_2$, 13682-74-1.

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(26) $Ni(CO)(\eta^2\text{-diene})(\eta^4\text{-diene})$, an intermediate similar to **8**, has been invoked to explain the photodimerization of dienes in the presence of $Ni(CO)_4$. However, it was postulated that this intermediate was formed dissociatively by the photolysis of $Ni(CO)_2(\eta^4\text{-diene})$. Hill, B.; Math, K.; Pillsbury, D.; Voecks, G.; Jennings, W. *Mol. Photochem.* **1973**, *5*, 195.

(27) E.g.: Bell, L. K.; Larkworthy, L. F.; Mason, J.; Mingos, D. M. P.; Tew, D. G.; Povey, D. C.; Sandell, B. *J. Chem. Soc., Chem. Commun.* **1983**, 125.

(28) For a recent review see: Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277.

(29) A reviewer has suggested that $Co(CO)(NO)(\eta^2\text{-}C_4H_6)_2$ might be particularly photosensitive. Our failure to observe the compound would be the result of the compound being destroyed by our UV lamp. This seems unlikely, since there is no evidence for a photostationary state in our experiments. Neither have we observed other $Co(CO)(NO)(L)_2$ species (L = olefin or N_2) in our experiments.[9,12] Equally it seems improbable that $Co(CO)(NO)(\eta^2\text{-}C_4H_6)_2$ could be so insoluble in LXe that we would be unable to detect its formation.