γ-alumina[18] in an ultrapure helium-flow reactor.[9] An advantage of this technique is that CO evolution can be measured directly. The reactor is sealed under helium and taken into a Vacuum Atmospheres drybox where the supported carbonyl is transferred under nitrogen to a Kel-F bullet type sleeve rotor that is sealed with Plasticine.[19] Samples prepared in this manner show no deterioration by NMR over a period of several days.[20] A typical set of CP MAS ^{13}C NMR spectra for molybdenum hexacarbonyl supported on partially dehydroxylated alumina under various conditions are shown in Figure 1.[21,22]

Spectrum A shows the result of activation for 1 h at 30 °C. Samples activated at this temperature are bright yellow. The CP MAS ^{13}C NMR spectrum shows one resonance in the carbonyl region at 203 ppm.[23,24] This is 2 ppm downfield from $Mo(CO)_6$(phys), which is also present in the sample (vide infra). This we assign to $Mo(CO)_5$(ads), which is proposed by Brenner and Burwell as an intermediate in the formation of $Mo(CO)_3$(ads).[5] This species should have an octahedral coordination geometry with a surface hydroxyl group occupying the sixth coordination site at molybdenum. If this is the case, then we expect to see the axial and equatorial carbonyl ligands in a ratio of 1:4. Our failure to see a unique axial resonance is due either to an accidental degeneracy of signals or to a dynamic process involving axial–equatorial CO exchange. Preliminary low-temperature NMR results show slight broadening of this resonance at −40 °C, which may be consistent with a dynamic process.

Activation of $Mo(CO)_6$ on alumina at 100 °C for 1 and 3 h leads to spectra B and C, respectively. Both of these samples are yellow-brown. A new broad resonance can be seen to grow at 223 ppm. This we assign to $Mo(CO)_3$(ads), again after Brenner and Burwell.[5] The chemical shift of this species corresponds well to literature values for (arene)$Mo(CO)_3$.[24] One resonance is expected if the group has C_{3v} symmetry, two are expected if the group has only mirror-plane symmetry, and three resonances are expected for a tricarbonyl group with no symmetry. On partially dehydroxylated alumina, it is difficult to imagine $Mo(CO)_3$(ads) at sites with threefold rotational symmetry. Thus more than one resonance should result for this species. Our results suggest a fluxional tricarbonyl group. This is well precedented for metal tricarbonyl fragments.[25]

The tricarbonyl group, $Mo(CO)_3$(ads), has in some cases been postulated to be dimeric; i.e., $Mo_2(CO)_6$(ads).[12,13] Comparison of model compounds $Cp_2Mo_2(CO)_6$[23] and (arene)$Mo(CO)_3$ shows chemical shifts of 228.6 and ~222 ppm, respectively. Furthermore, the latter compound shows coalescence of carbonyl resonances at temperatures below 0 °C while the former shows coalescence close to 100 °C. Although this is not proof, certainly the results for $Mo(CO)_3$(ads) more closely resemble the mononuclear model complexes.

When the NMR spectra of samples A–C are recorded by using a single carbon 90° pulse with or without proton decoupling (i.e., no cross polarization), residual physisorbed $Mo(CO)_6$ is observed at 201 ppm in each sample. The presence of residual $Mo(CO)_6$ is probably a function of our reaction conditions. The NMR samples contain nearly monlayer coverage by molybdenum subcarbonyl.[21] For these high coverages the reaction times used were not sufficient to completely convert to the tricarbonyl. Also, a relatively low helium sweep rate (30 mL/min) was used in these reactions. This is consistent with the equilibrium postulated by Brenner and Burwell (eq 1).[5] If the reaction is stopped prematurely,

$$Mo(CO)_6(\text{phys}) \underset{+CO}{\overset{-CO}{\rightleftarrows}} Mo(CO)_5(\text{ads}) \underset{+CO}{\overset{-CO}{\rightleftarrows}} Mo(CO)_3(\text{ads}) \quad (1)$$

then $Mo(CO)_6$(phys) can be generated in the sealed rotor. Furthermore, we can confirm that on small samples and low weight percent loadings (250 mg of alumina, <2 wt % $Mo(CO)_6$) nearly 3 equiv of CO/equiv of Mo is evolved at 100 °C after 2 h.[26]

The NMR results for $Mo(CO)_6$ decomposed on hydroxylated alumina are substantially the same as reported for partially dehydroxylated alumina. However, for $Mo(CO)_6$ on dehydroxylated alumina, we find that $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads) cannot be detected by MAS NMR. This is due to the obvious lack of nearby protons for cross polarization experiments and an apparent increase in T_1 caused by anchoring the subcarbonyl to the surface. On dehydroxylated alumina we can easily obtain a spectrum for $Mo(CO)_6$(phys) using the single-pulse sequence described above. The chemical shift is the same as for $Mo(CO)_6$(phys) on partially dehydroxylated alumina, i.e. 201 ppm.

Acknowledgment. Support of this work was provided by the National Science Foundation (Grant DMR 82-11111). We thank Professor R. L. Burwell, Jr., for his generous hospitality during a visit by B.E.H. to Northwestern University and for advice on the construction of a helium-flow reactor.

Registry No. $Mo(CO)_6$, 13939-06-5; alumina, 1344-28-1.

---

[19] Plasticine is modeling material manufactured by Colorforms, Ramsey, NJ 07446.

[20] The samples did not bleach over a period of 4 days when prepared in this fashion, and the spectrum obtained on an aged sample gave the same relative intensity for the observed signals. Samples exposed directly to air bleached within a few minutes.

[21] All NMR samples were prepared to contain a monolayer of molybdenum carbonyl, ca. 6 wt. % $Mo(CO)_6$,[4] by impregnation from pentane solution. Excess $Mo(CO)_6$ was removed by sublimation in flowing helium at 25 °C.

[22] NMR spectra were recorded on a JEOL FX60Q-S spectrometer. The solids accessory was manufactured by Chemagnetics.

[23] This correlates well with monosubstituted molybdenum carbonyl derivatives $LMo(CO)_5$.[24]

[24] Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

[25] Cotton, F. A.; Hanson, B. E. *Isr. J. Chem.* **1976**, *15*, 165.

[26] The average value for five runs in which the loading was between 0.8 and 1.8 wt % $Mo(CO)_6$ was 2.95 ± 0.06 equiv of CO/equiv of Mo.

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Brian E. Hanson*
George W. Wagner
Robert J. Davis
Edwin Motell

Received October 28, 1983

Iridium–Nitrogen Bond Cleavage in the Photolysis of Carbonylnitrosylbis(triphenylphosphine)iridium

Sir:

The identification of metal isocyanate (M–NCO) species on metal surfaces has led to the proposal of their involvement as intermediates in the metal-catalyzed pollution removal reaction of nitric oxide and carbon monoxide as ammonia and carbon dioxide.[1] A homogeneous model for isocyanate formation from the interaction of CO and NO at a metal site is reaction 1.[2] This reaction has been proposed to proceed

$$[Pt(PEt_3)_2(NO)(NO_2)] + 2CO \rightarrow \underset{\mathbf{2}}{[Pt(PEt_3)_2(NCO)(NO_2)]} + CO_2 \quad (1)$$

---

[1] (a) Unland, M. L. *Science* **1973**, *179*, 567. (b) Unland, M. L. *J. Phys. Chem.* **1973**, *77*, 1952. (c) Unland, M. L. *J. Catal.* **1973**, *31*, 459.

[2] Bhaduri, S. A.; Bratt, I.; Johnson, B. F. G.; Khair, A.; Segal, J. A.; Walters, R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1981**, 234.

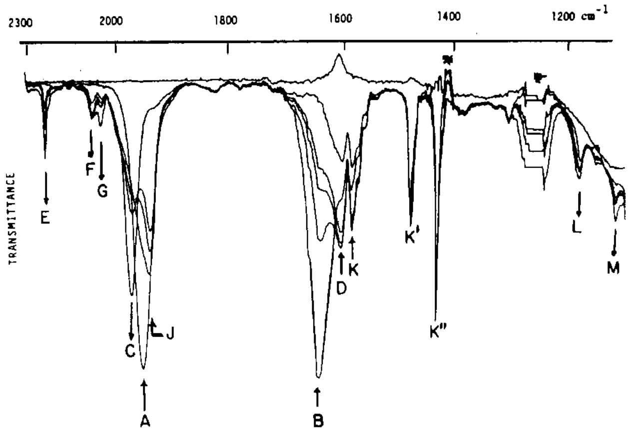

Figure 1. IR spectra showing the photolysis of a solution of $[\mathrm{Ir(PPh_3)_2(CO)(NO)}]$ (0.003 M) and $\mathrm{PPh_3}$ (0.02 M) in $\mathrm{CH_2Cl_2}$. Photolysis time: 0, 300 s, 600 s, 900 s, 1680 s (asterisks mark regions where solvent transmittance is low).

through a nitrene intermediate similar to that proposed for the photochemical reaction (2).[3] The intramolecular capture

$$\underset{1}{[\mathrm{Ir(PPh_3)_2(CO)(NO)}]} + 2\mathrm{PPh_3} \xrightarrow{h\nu} \underset{2}{[\mathrm{Ir(PPh_3)_3(NCO)}]} + \mathrm{Ph_3PO} \quad (2)$$

of a bonded CO ligand by a nitrene intermediate has been previously reported in the formation of isocyanate complexes in the photolyses of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2(\mathrm{NO})]$ and $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{PPh_3})\mathrm{N_3}]$ in the presence of $\mathrm{PPh_3}$.[4] While thermal reactions of azido carbonyl and thiocarbonyl complexes **3** (M = Ir, Rh; X = O, S) with CO also give isocyanato and isothiocyanato complexes, **4**,[5] we have observed that

$$\underset{3}{[\mathrm{M(PPh_3)_2(CX)N_3}]} + \mathrm{CO} \rightarrow \underset{4}{[\mathrm{M(PPh_3)_2(CO)(NCX)}]} + \mathrm{N_2} \quad (3)$$

thermal and photochemical reactions of *trans*-$[\mathrm{M(PPh_3)_2(CO)(N_3)}]$ in the presence of $\mathrm{PPh_3}$ do not give the isocyanato products $[\mathrm{M(PPh_3)_3NCO}]$ which would be expected from the intramolecular capture of a bonded CO by a nitrene fragment analogous to reaction 2. Moreover, since dinitrogen should be a better leaving group in **3** than "O" from the NO group in **1**, it was of importance to reexamine the previously reported photoinduced reaction (2). We describe photolytic experiments with $[\mathrm{Ir(PPh_3)_2(CO)(NO)}]$ in a variety of solvents under a variety of conditions which, contrary to the previous report, indicate that the isocyanato complex **2** is not formed; rather, the primary process is the cleavage of the Ir–N bond in $[\mathrm{Ir(NO)(PPh_3)_2(CO)}]$.

The photolysis of $[\mathrm{Ir(PPh_3)_2(CO)(NO)}]$ (**1**) and $\mathrm{PPh_3}$ in dichloromethane using Pyrex-filtered radiation (>300 nm) was monitored by the IR spectra that were recorded against the same concentration of $\mathrm{PPh_3}$ in $\mathrm{CH_2Cl_2}$ in the reference cell. The growth and decay of IR bands during the course of photolysis are shown by arrows in Figure 1. The relevant spectral frequencies are identified in the Figure and in the text by capital letters. After irradiation in a stoppered infrared cell for 300 s, the intensities of the 1944-$\mathrm{cm^{-1}}$ ν(CO) (A) and 1638-$\mathrm{cm^{-1}}$ ν(NO) (B) bands of **1** decreased with formation of bands at 1932 $\mathrm{cm^{-1}}$ (J) and 1599 $\mathrm{cm^{-1}}$ (D). Photolysis for an additional 300 s leads to further diminution of the intensities of the 1638-$\mathrm{cm^{-1}}$ (B) band and the 1932-$\mathrm{cm^{-1}}$ (J) band with a shoulder appearing at 1964 $\mathrm{cm^{-1}}$ (C). Photolysis for an additional 1080 s leads to complete decay of the 1932-$\mathrm{cm^{-1}}$ (J) and 1638-$\mathrm{cm^{-1}}$ (B) bands with further enhancement of the 1964-$\mathrm{cm^{-1}}$ (C) band. The absorption bands at 1585 $\mathrm{cm^{-1}}$ (K), 1480 $\mathrm{cm^{-1}}$ (K′), and 1435 $\mathrm{cm^{-1}}$ (K″) due to coordinated $\mathrm{PPh_3}$ in **1** remain relatively unchanged. Throughout the course of the photolysis, the intensities of the weak bands at 2223 $\mathrm{cm^{-1}}$ (E), 2060 $\mathrm{cm^{-1}}$ (F), 2032 $\mathrm{cm^{-1}}$ (G), 1187 $\mathrm{cm^{-1}}$ (L), and 1120 $\mathrm{cm^{-1}}$ (M) were observed to increase slowly. Additionally, a very weak band at 2339 $\mathrm{cm^{-1}}$ due to $\mathrm{CO_2}$ was observed.

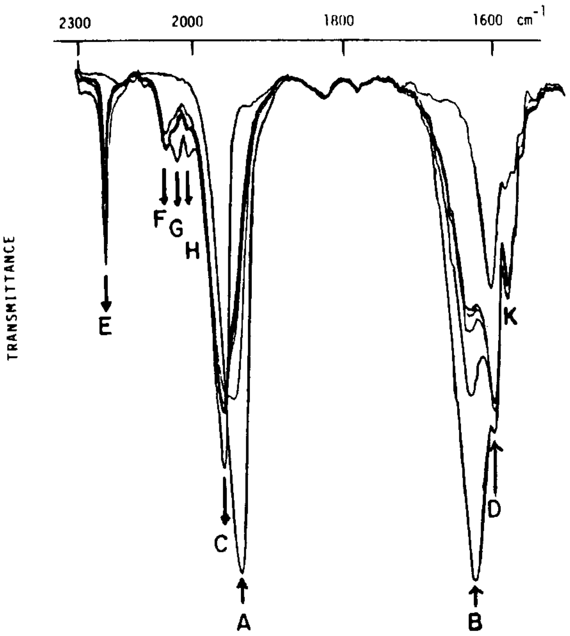

Figure 2. IR spectra showing the photolysis of a solution of $[\mathrm{Ir(PPh_3)_2(CO)(NO)}]$ (0.003 M) in $\mathrm{CH_2Cl_2}$. Photolysis time: 0, 300 s, 600 s, 900 s, 1200 s, 2100 s.

Assignments of the IR frequencies of the photolytic products were accomplished with the aid of the following experiments. A solution of $\mathrm{PPh_3}$ in dichloromethane was briefly treated with nitric oxide to form $\mathrm{N_2O}$, which was characterized by the 2223-$\mathrm{cm^{-1}}$ (E) band, and $\mathrm{Ph_3PO}$, which was characterized by the 1185-$\mathrm{cm^{-1}}$ (L) and 1120-$\mathrm{cm^{-1}}$ (M) bands.[6] Further confirmation of the assignment of the 2223-$\mathrm{cm^{-1}}$ (E) band to $\mathrm{N_2O}$ was established by noting the diminution of the intensity of the E band when the photolyzed solution was purged with nitrogen and also by comparison with the spectrum of an authentic sample of $\mathrm{N_2O}$ in dichloromethane. To ensure that the 2223-$\mathrm{cm^{-1}}$ (E) band was not due to $[\mathrm{Ir(PPh_3)_3(NCO)}]$, a solution of $[\mathrm{Ir(PPh_3)_2(CO)(NO)}]$ in $\mathrm{CH_2Cl_2}$ was photolyzed and then treated with CO to convert any $[\mathrm{Ir(PPh_3)_3NCO}]$ formed to $[\mathrm{Ir(PPh_2)_2(CO)(NCO)}]$.[7] The IR spectrum of this solution showed the absence of the characteristic 2240-$\mathrm{cm^{-1}}$ NCO band present in the spectrum of an authentic sample of $[\mathrm{Ir(PPh_3)_2(CO)(NCO)}]$. This isocyanate was found also not to undergo photolytic decomposition upon irradiation for 25 min.

The strong 1964-$\mathrm{cm^{-1}}$ (C) band is assigned to *trans*-$[\mathrm{Ir(PPh_3)_2(CO)Cl}]$ on the basis of comparison with the spectrum of an authentic sample of *trans*-$[\mathrm{Ir(PPh_3)_2(CO)Cl}]$ in dichloromethane and also by its isolation from photolysis of a more concentrated solution. The very weak IR bands at 2060 $\mathrm{cm^{-1}}$ (F) and 2032 $\mathrm{cm^{-1}}$ (G) are in the region where iridium(III) carbonyl complexes have absorption bands. The weak

---

(3) Bhaduri, S. A.; Johnson, B. F. G.; Savory, C. J.; Segal, J. A.; Walter, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 809.

(4) McPhail, A. T.; Knox, G. R.; Robertson, C. G.; Sim, G. A. *J. Chem. Soc. A* **1971**, 205.

(5) Kubota, M.; Chappell, T. G. *J. Chem. Soc., Dalton Trans.* **1979**, 406 and references therein.

(6) Longhi, R.; Ragsdale, R. O.; Drago, R. S. *Inorg. Chem.* **1962**, *1*, 768.

(7) Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

band at 1599 cm^{-1} (D) is due to the thermal PPh_3 substitution product, $[Ir(PPh_3)_3(NO)]$.[9] The only IR band that remains to be accounted for is the absorption at 1932 cm^{-1} (J), which is rapidly formed but decays upon photolysis. While we were unable to isolate a species that has absorption at 1932 cm^{-1}, which is in the region expected for an Ir(I) carbonyl, a species with increased extent of back-bonding to CO would be $[Ir(PPh_3)_3(CO)]$.

Since the course of photolysis shown by the IR changes in Figure 1 does not proceed with concurrent diminution of IR bands due to CO and NO stretching in the 1944- and 1638-cm^{-1} regions with concomitant appearance of a band at 2240 cm^{-1} due to NCO, it is certain that the photolytic reaction does not proceed as shown by eq 2. It is likely that the previous investigators assumed that the band at 2223 cm^{-1} was due to an isocyanate complex, and not to N_2O as we have convincingly confirmed.

A reasonable sequence of reactions that accounts for the major products observed in the photolysis is shown in (4).

$$[Ir(PPh_3)_2(CO)(NO)] \xrightarrow{h\nu} [Ir(PPh_3)_2(CO)(NO)]^* \quad (4a)$$

$$[Ir(PPh_3)_2(CO)(NO)]^* \rightarrow [\cdot Ir(PPh_3)_2(CO)] + \cdot NO \quad (4b)$$

$$[\cdot Ir(PPh_3)_2(CO)] + PPh_3 \rightleftarrows [\cdot Ir(PPh_3)_3(CO)] \quad (4c)$$

$$2NO\cdot + PPh_3 \rightarrow N_2O + Ph_3PO \quad (4d)$$

$$[\cdot Ir(PPh_3)_2(CO)] + CH_2Cl_2 \rightarrow [Ir(PPh_3)_2(CO)Cl] + CH_2Cl\cdot \quad (4e)$$

The $CH_2Cl\cdot$ radical would undergo further radical chain termination steps. We also note that the reaction of NO with PPh_3 was too rapid to allow observation of NO in the presence of excess PPh_3. The thermal stability of $[Ir(PPh_3)_2(CO)(NO)]$ was established by observing no reaction of this compound upon refluxing for 6 h in CH_2Cl_2 or in $CHCl_3$.

The course of photolysis of $[Ir(PPh_3)_2(CO)(NO)]$ (**1**) in CH_2Cl_2 in the absence of added PPh_3 using Pyrex-filtered radiation (>300 nm) is shown by the IR spectra presented in Figure 2. Photolysis for 300 s leads to diminution of the 1940-cm^{-1} ν(CO) (A) and 1638-cm^{-1} ν(NO) (B) bands of **1** accompanied by development of shoulders at 1963 cm^{-1} (C) and 1605 cm^{-1} (D) and growth of weak bands at 2223 cm^{-1} (E), 2060 cm^{-1} (F), and 2339 cm^{-1} (due to CO_2). After photolysis for 2100 s, the strong A and B bands due to **1** were replaced by a strong band at 1963 cm^{-1} (C), medium bands at 2223 cm^{-1} (E) and 1605 cm^{-1} (D), and very weak bands at 2060 cm^{-1} (F), 2032 cm^{-1} (G), and 2000 cm^{-1} (H). The intermediate species with absorption at 1932 cm^{-1} (J), which was observed in the photolysis of **1** in the presence of PPh_3, was not observed. The primary product characterized by the 1963-cm^{-1} (C) band was $[Ir(PPh_3)_2(CO)Cl]$ formed by the reaction of $[\cdot Ir(PPh_3)_2(CO)]$ with the solvent CH_2Cl_2. The formation of N_2O shown by the growth of the 2223-cm^{-1} (E) band may be due to the reaction of NO with $[Ir(PPh_3)_2(CO)Cl]$[10] or $[Ir(PPh_3)_2(CO)(NO)]$.[11] The small amounts of CO_2 (2339 cm^{-1}) observed are due to the metal-catalyzed reaction of CO and NO.[10]

Photolysis of a solution of $[Ir(PPh_3)_2(CO)(NO)]$ (**1**) and PPh_3 in CH_2Cl_2 using a medium-pressure Hg lamp with a quartz jacket leads to rapid decomposition of **1** and formation of $[Ir(PPh_3)_2(CO)Cl]$, which is shown by a weak band at 1965 cm^{-1}. This compound was also decomposed within 1200 s. The formation of N_2O was indicated by a weak band at 2223 cm^{-1} and Ph_3PO by bands at 1191 and 1128 cm^{-1}. The growth of a weak band at 2339 cm^{-1} also indicated the formation of CO_2. Noteworthy, again, was the lack of formation of an isocyanato species with absorption at 2240 cm^{-1} concomitant with the decay of ν(CO) and ν(NO) bands.

A photolytic survey using Pyrex- or quartz-filtered irradiation of solutions of $[Ir(PPh_3)_2(CO)(NO)]$ and PPh_3 in solvents such as $CHCl_3$, benzene, CH_3CN, or toluene also gave no indication of the formation of $[Ir(PPh_3)_3(NCO)]$. The formation of Ph_3PO from the reaction of PPh_3 and photodissociated NO was indicated in these photolyses. Compared to the thermal reactions of $[Ir(PPh_3)_2(CO)(NO)]$ with PPh_3, which gives $[Ir(PPh_3)_3(NO)]$,[9] the present study indicates that the photoinduced reaction proceeds with cleavage of the Ir–NO bond.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1**, 39014-32-9; *trans*-$[Ir(PPh_3)_2(CO)Cl]$, 15318-31-7; PPh_3, 603-35-0; Ph_3PO, 791-28-6; N_2O, 10024-97-2; CH_2Cl_2, 75-09-2.

Department of Chemistry
Harvey Mudd College
Claremont, California 91711

Mitsuru Kubota*
Michael K. Chan
L. Keith Woo

Received January 13, 1984

---

(8) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368.
(9) Reed, C. A.; Roper, W. R. *J. Chem. Soc. A* **1970**, 3054.
(10) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3325.
(11) Angoletta, M. *Gazz. Chim. Ital.* **1963**, *93*, 1591.