# Matrix Photolysis of $[(\eta^5\text{-}C_5H_5)W(CO)_2NO]$: An Intramolecular Formation of an Isocyanate Ligand

**Ramli B. Hitam,[a] Antony J. Rest,*[a] Max Herberhold,*[b] and Walter Kremnitz[b]**

[a] *Department of Chemistry, The University, Southampton SO9 5NH, U.K.*
[b] *Laboratorium für Anorganische Chemie der Universität, Postfach 3008, D-8580 Bayreuth, West Germany*

Matrix isolation evidence from $[(\eta^5\text{-}C_5H_5)W(CO)_2NO]$ (**1a**) and its labelled analogues containing $^{13}CO$, $C^{18}O$, or $N^{18}O$ indicates an intramolecular CO attack at the nitrogen of a NO ligand in the photochemical formation of a group 6 metal isocyanato-species.

The light-sensitive half-sandwich complexes $[CpM(CO)_2NO]$ [Cp = $\eta^5$-cyclopentadienyl, $\eta^5\text{-}C_5H_5$; M = Cr, Mo; W (**1a**)] are currently being investigated as precursors to the optically active compounds [CpM(CO)(L)NO] (L = two-electron ligand).[1] Photolysis of $[CpM(CO)_2NO]$ complexes in low temperature matrices leads initially to dissociative loss of a single CO ligand; the co-ordinatively unsaturated 16-electron species [CpM(CO)(NO)] [M = Cr,[2] Mo; W,[3] (**2a**)] have been characterised at 12 K in various gas matrices (Ar, $CH_4$, CO, $N_2$). However, the photo-induced substitution of a CO ligand in solution has only been used synthetically in the case of Cr. Complexes of the type [CpCr(CO)(L)(NO)] have been obtained with phosphorus-[4,5] and nitrogen-[5] containing ligands as well as with alkenes and alkynes.[6,7] In the cases of Mo and W, the photoreactions are much slower and often involve both side-reactions and decompositions.† For example, u.v. photolysis of $[CpMo(CO)_2NO]$ in benzene in the presence of $PPh_3$ yielded, in addition to the expected monosubstituted derivative $[CpMo(CO)(PPh_3)NO]$, a novel isocyanate complex $[CpMo(CO)(PPh_3)_2(NCO)]$ whose structure was verified by *X*-ray crystallography.[9] The formation of the isocyanate ligand was proposed to proceed *via* a nitrene species which captured a CO ligand.[9] In this communication we report definitive evidence from matrix isolation experiments with isotopic labelling which confirms that isocyanate

---

† The lower photoreactivity of $[CpM(CO)_2NO]$ [M = Mo; W (**1a**)] may be seen from the fact that these complexes can be synthesised in high yield by photolysis of a benzene solution of $\{[CpM(CO)_3]_2\}$ in the presence of NO gas.[8]

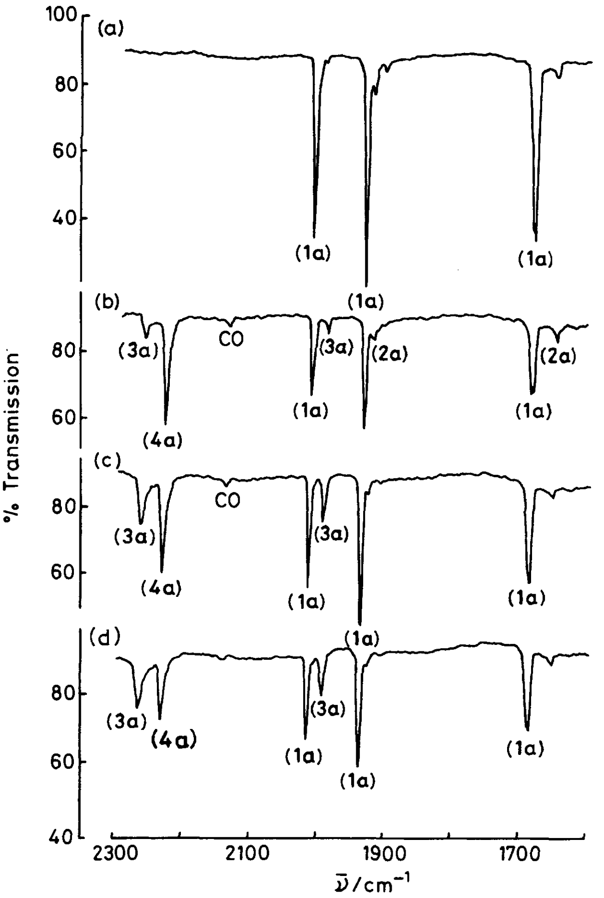


**Figure 1.** I.r. spectra from an experiment with [CpW(CO)$_2$NO] (**1a**) isolated at high dilution in an argon matrix (1 : 2000 to 1 : 5000) at *ca.* 12 K: (a) after deposition; (b) after 30 min photolysis ($\lambda < 370$ and $\lambda > 550$ nm); (c) after further 120 min visible light photolysis ($\lambda > 520$ nm); and (d) after annealing to *ca.* 35 K.

ligand formation involves intramolecular migration of a CO ligand.

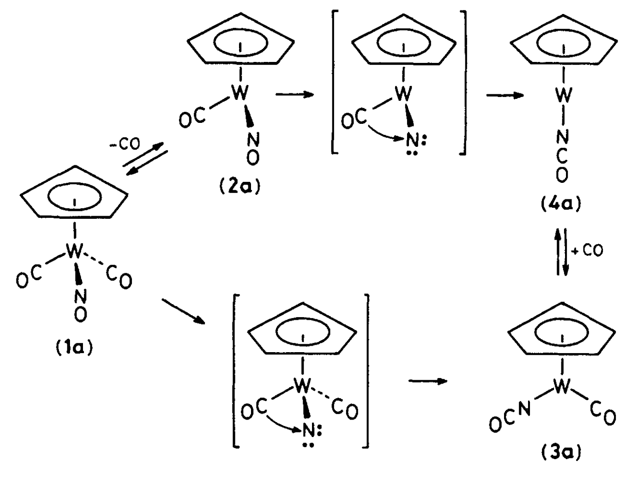
Figure 1 presents the i.r. spectra which were observed upon irradiation of [CpW(CO)$_2$NO] (**1a**), isolated at high dilution in an Ar matrix at 12 K. Photolysis ($\lambda < 370$ and $\lambda > 550$ nm)‡ of (**1a**) [Figure 1(a)] produced six new bands [Figure 1(b)] which indicated the formation of three complexes [(**2a**), (**3a**), and (**4a**), Table 1] in addition to carbon monoxide (2138 cm$^{-1}$). From separate narrower wavelength photolyses ($290 < \lambda < 370$ nm) with [CpM(CO)$_2$NO] complexes [M = Cr,[2] Mo; W,[3] (**1a**)], the weak absorptions at 1923.8 and 1652.8 cm$^{-1}$ can be unequivocally assigned to the CO-deficient species [CpW(CO)(NO)] (**2a**).

On irradiating with visible light ($\lambda > 520$ nm) the bands corresponding to (**2a**) decreased while those of (**1a**) gained in intensity. At the same time, the two absorptions at 2265.7 and 1995.9 cm$^{-1}$, assigned to the new species (**3a**), increased at the expense of the band at 2233.7 cm$^{-1}$, assigned to the new species (**4a**) [Figure 1(c)]. On annealing the matrix to *ca.* 35 K a further decrease of (**4a**) with a concomitant increase of (**3a**) occurred [Figure 1(d)]. From the behaviour of the bands under the given experimental conditions of high dilution it can be concluded that all three photoproducts (**2a**)—(**4a**) are mononuclear. Of the three absorptions belonging to (**3a**) and (**4a**), the band at 1995.9 cm$^{-1}$ can be confidently assigned as a terminal CO stretching mode while the two bands above 2200 cm$^{-1}$ may be correlated with the antisymmetric stretching modes of isocyanate ligands ($\nu_{as}$ at 2200—2300 cm$^{-1}$),[10] in accordance with the photo-induced formation of [CpMo(CO)(PPh$_3$)$_2$(NCO)] ($\nu_{as}$ 2225 cm$^{-1}$ in CHCl$_3$).[9]

**Table 1.** Infrared band positions (cm$^{-1}$) of [CpW(CO)$_2$NO] (**1a**) and its photoproducts in argon matrices.

| Complex | $\nu_{as}$(NCO) | $\nu$(CO) | $\nu$(NO) |
|---|---|---|---|
| [CpW(CO)$_2$NO] (**1a**) | | 2015.9, 1938.7 | 1688.5$^a$ |
| [CpW(CO)NO] (**2a**) | | 1923.8 | 1652.8 |
| [CpW(CO)(NCO)] (**3a**) | 2265.7 | 1995.9 | |
| [CpW(NCO)] (**4a**) | 2233.7 | | |
| [CpW($^{13}$CO)NO] (**2b**) | | 1884.6 | 1652.8 |
| [CpW($^{13}$CO)(N$^{13}$CO)] (**3b**) | 2203.9 | 1969.9 | |
| [CpW(N$^{13}$CO)] (**4b**) | 2172.8 | | |
| [CpW(C$^{18}$O)NO] (**2c**) | | 1878.3 | 1652.8 |
| [CpW(C$^{18}$O)(NC$^{18}$O)] (**3c**) | 2252.2 | 1950.0 | |
| [CpW(NC$^{18}$O)] (**4c**) | 2218.2 | | |

$^a$ Matrix-split doublet (1686.7 and 1690.3 cm$^{-1}$).



**Scheme 1**

The identities of (**3a**) and (**4a**) were established by experiments with the labelled complexes§ [CpW($^{12}$CO)$_{2-n}$($^{13}$CO)$_n$NO] (**1b**), [CpW(C$^{16}$O)$_{2-n}$(C$^{18}$O)$_n$NO] (**1c**), and (CpW(CO)$_2$(N$^{18}$O)] (**1d**), isolated in Ar matrices at 12 K. Irradiation of the $^{13}$CO enriched starting complex gave four additional bands with wavenumbers appropriate for the $^{12}$C/$^{13}$C shift of the bands of (**2a**), (**3a**), and (**4a**), and the bands are therefore assigned to (**2b**), (**3b**), and (**4b**) (Table 1). The fact that only three new bands are seen for (**3b**) and (**4b**) establishes that there are single C atoms in the ligands of (**3a**) and (**4a**), *i.e.* (**3a**) and (**4a**) are probably [CpW(CO)(NCO)] and [CpW(NCO)], respectively. The experiment with the C$^{18}$O enriched complex again gave four new bands, corresponding to (**2c**), (**3c**), and (**4c**) (Table 1), thus indicating the presence of single O atoms in the ligands. A comparison of the $^{13}$CO with the C$^{18}$O experiment can be used to confirm the identity of the isocyanate ligands, since only small shifts in the upper wavenumber bands were observed for the C$^{18}$O

---

‡ Details of the 12 K cryostat, vacuum systems, spectrometers, wavelength selective photolysis filters, and matrix gases are described elsewhere.[2,3]

§ The syntheses of the labelled compounds will be given elsewhere.[3]

labelled complexes (**3c**) and (**4c**) in contrast to the large shifts for the $^{13}CO$ labelled compounds (**3b**) and (**4b**) (Table 1); there is only a small contributory motion of the O atom in the antisymmetric stretching vibration but a larger motion of the C atom. Significantly, irradiation of the $N^{18}O$ enriched complex resulted in no new bands which might correspond to $^{18}O$ labelled isocyanate complexes, *i.e.* the O atom in the isocyanate ligand does not come from the NO ligand.

In conclusion, the matrix isolation experiments with (**1a**) and involving isotopic labelling have established for the first time that isocyanate ligands, NCO, can be formed within the co-ordination sphere of a metal from CO and NO ligands and that the CO component originates from the CO ligand. The observation of two different isocyanate species, (**3a**) and (**4a**), means that it is not possible to choose unambiguously between the two paths illustrated in Scheme 1. The i.r. evidence, however, favours the path *via* [CpW(CO)(NO)] (**2a**).

Surprisingly, no evidence for the production of $CO_2$ has been observed in these matrix experiments; the O atom would be expected to react with photo-ejected CO in the matrix cage.

The Southampton group thank the Universiti Teknologi Malaysia for a Studentship (to R. B. H.) and the S.E.R.C. for support (to A. J. R.). The Bayreuth group thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support (to M. H.).

*Received, 28th October 1983; Com 1414*

## References

1 H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 151.

2 M. Herberhold, W. Kremnitz, H. Trampisch, R. B. Hitam, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 1261.

3 R. B. Hitam, A. J. Rest, M. Herberhold, and W. Kremnitz, in preparation.

4 H. Brunner, *J. Organomet. Chem.*, 1969, **16**, 119.

5 M. Herberhold and H. G. Alt, *Liebigs Ann. Chem.*, 1976, 292.

6 M. Herberhold and H. G. Alt, *J. Organomet. Chem.*, 1972, **42**, 407.

7 M. Herberhold, H. G. Alt, and C. G. Kreiter, *Liebigs Ann. Chem.*, 1976, 300.

8 A. M. Rosan and J. W. Faller, *Synth. React. Inorg. Metal-Org. Chem.*, 1976, **6**, 357.

9 A. T. McPhail, P. M. Gross, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc. A*, 1971, 205.

10 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1978.