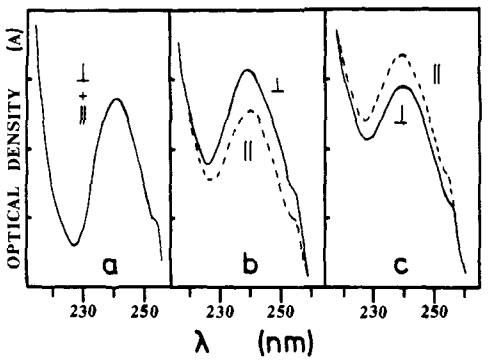

Figure 1. Uv band of $Fe(CO)_5$ trapped in a matrix of solid CO at 20 K (ratio 1:500): (a) superimposed spectra with plane polarized light ∥ and ⊥, following deposition from gas phase; (b) spectra after 4.5 h photolysis with λ 255 nm ∥ radiation; (c) spectra after 2 h photolysis with ⊥ radiation.

performed a similar experiment with d^8 iron pentacarbonyl and have produced a partially oriented sample of $Fe(CO)_5$ in solid carbon monoxide at 20 K.

Figure 1a shows part of the visible/uv spectrum between 220 and 260 nm of $Fe(CO)_5$ matrix isolated in CO at 20 K (dilution 1:500). Gray and co-workers have assigned[5] the band centered at 240 nm to the transition $^1A_1' \rightarrow {}^1E'$ (i.e., a transition moment of species e'). The gas phase deposited sample is randomly oriented since spectra recorded with light polarized in two perpendicular directions (we label these ∥ and ⊥ for clarity) are superimposable. Similarly, the two ir bands in the "carbonyl stretching" region (of symmetry species e' and a_2'') display constant intensities when recorded in the two different polarizations. Figure 1b shows the same region of the uv spectrum of the sample recorded under identical conditions but after 4.5 h of polarized (∥) photolysis with λ 255 nm (mercury lamp + monochromator + polarizer). The spectral intensity now clearly depends upon polarizer orientation. Figure 1c shows the same spectral region after 2 h photolysis with light of the same wavelength but opposite polarization (⊥). The band intensity behavior is the opposite to that of Figure 1b. Similar polarization effects are seen in the infrared spectrum with the polarization effect ($I_\parallel/I_\perp$) being in the opposite direction for the two ir bands of different symmetry. The polarization behavior of the uv band at 240 nm during the polarized photolysis mirrors that of the e' carbonyl stretching vibration, but is opposite to that of the a_2'' vibration, thus confirming Gray et al.'s assignment[5] (i.e., transition moment of species e').

The overall effect of the polarized photolysis is to move the $Fe(CO)_5$ molecules to positions where they have a lower chance of absorbing light of this particular polarization. We discuss possible mechanisms elsewhere[6] but note that in inert matrices (Ar, Xe, CH_4 etc.) photolysis of matrix isolated $Fe(CO)_5$ at this wavelength leads to the formation of the $Fe(CO)_4$ fragment. Essentially no $Fe(CO)_4$ is detected in solid CO because of the ready recombination of $Fe(CO)_4$ and CO.[7]

$$Fe(CO)_5 \xrightarrow[CO]{h\nu} Fe(CO)_4 + CO \xrightarrow{\text{recombination}} Fe(CO)_5$$

The reorientation step may thus either take place during photolysis, during recombination of $Fe(CO)_4$ with the excess CO, or as an intramolecular rearrangement of $Fe(CO)_4$ itself.

However, knowledge of the exact mechanism is immaterial to the main point. No change in the polarization properties of the system was found during several hours of spectroscopic observation of the sample. If $Fe(CO)_5$ were fluxional under these conditions (i.e., necessitating a continuously changing orientation) maintenance of polarization for more than a fraction of a second would be impossible. We can in fact put an upper limit of 10^{-4} s^{-1} on the frequency of any spontaneous process that alters the orientation of $Fe(CO)_5$ matrix isolated in CO at 20 K. Any process which rapidly exchanges ligands and leaves the direction of the figure axis of $Fe(CO)_5$ totally unaffected over several hours would require mutually contradictory properties of the matrix environment; i.e., three of the CO groups are clamped rigidly while the other two CO groups are freely moving. In general, we have no evidence for spontaneous intramolecular rearrangements in binary carbonyls $M(CO)_x$ (M = Fe, Cr) trapped in frozen inert gas matrices. We believe that rearrangements only occur in these systems within a matrix environment when energy is fed into the molecule (as in photolysis[6]). The number, frequency, and relative intensity of the carbonyl ir bands of these molecules allow ready calculation of the angular geometry about the central atom.[8] Asymmetric structures are observed for $Fe(CO)_4$[7] and $Mo(CO)_4$[9] (C_{2v}) and $Fe(CO)_3$[10] and $Mo(CO)_3$[9] (C_{3v}) and not the more regular structures (T_d and D_{3h}, respectively) which would be observed if the suggestion of Sheline and Mahnke[11] that these carbonyls may be fluxional on the infrared timescale was correct.

References and Notes

(1) B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **25**, 737 (1969).
(2) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans Faraday Soc.*, **58**, 1893 (1962).
(3) H. W. Spiess, R. Grosescu, and V. Haeberlen, *Chem. Phys.*, **6**, 226 (1974).
(4) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 157 (1975).
(5) M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *Bull. Soc. Chim. Fr.*, 4223 (1969).
(6) J. K. Burdett, I. R. Dunkin, J. M. Grzybowski, R. N. Perutz, M. Poliakoff, J. J. Turner, and R. F. Turner, to be submitted for publication.
(7) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).
(8) J. K. Burdett, H. Dubost, M. Poliakoff, and J. J. Turner in "Advances in IR and Raman Spectroscopy", Clark and Hester, Ed., Heyden, 1976.
(9) R. N. Perutz and J. J. Turner, *J. Am. Chem., Soc.*, **97**, 4800 (1975).
(10) M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 210 (1974).
(11) R. K. Sheline and H. Mahnke, *Angew. Chem., Int. Ed. Engl.*, **14**, 314 (1975).

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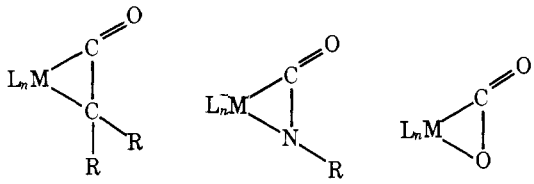
Synthesis and Structure of a Stable, Crystalline Complex of Methyl Isocyanate

Sir:

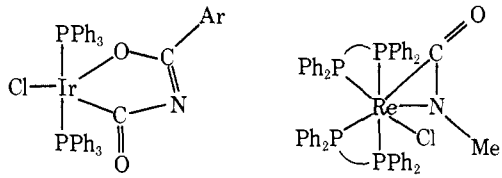
Whereas complexes of ketenes (**1**)[1] and carbon dioxide (**3**)[2] are now well established, no complex of a simple organic isocyanate has yet been adequately characterized. Complexes of *aroyl* isocyanates have been known for some time[3-5] but the neighboring carbonyl group can participate in the bonding so as to give a five-membered chelate ring (as in **4**) in which the isocyanate function is no longer recognizable. There is good evidence that this is what actually happens[5] and we can reinterpret the experimental results of Collman and his co-workers[3] as being more consistent with structure **4** than with structure **2** (R = ArCO) for the complexes $IrCl(ArCO{\cdot}NCO)(PPh_3)_2$. In particular, we think that it is significant that benzoyl isocyanate displaces dinitrogen from $IrCl(N_2)(PPh_3)_2$ to give **4** (Ar = Ph) but phenyl isocyanate does not.

We now describe the first example of a complex of an organic isocyanate which does not possess potential binding sites apart from those of the isocyanate function. The complex,

$ReCl(MeNCO)(dppe)_2$ (**5**), is shown to have structure **2** (R = Me) and it thus completes the series of three-membered metallocyclic ketones (**1**–**3**). Sulfur is a better donor than oxygen towards the softer metals and complexes of carbon disulfide[6] and organic isothiocyanates[7] are well known. We are not aware of the existence of coordinated thioketenes.

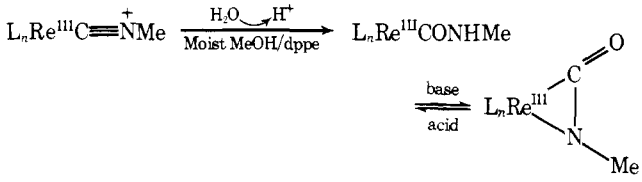


1 **2** **3**



4 **5**

The complex **5** was synthesized by the following sequence of reactions:



Methyl isocyanide (12.9 mmol) in degassed benzene (25 ml) was added dropwise from a pressure equalizing funnel over 4 h to a vigorously stirred suspension of *trans*-$ReOCl_3(PPh_3)_2$ (6.4 mmol) and triphenylphosphine (20.0 mmol) in degassed dichloromethane (120 ml) under nitrogen. The resulting amber solution was concentrated to 20 ml at room temperature and then shaken with acetonitrile (15 ml) and benzene (15 ml) to give orange crystals of the complex $ReCl_3(MeNC)(PPh_3)_2$ in 92% yield. The product was recrystallized by adding methanol or benzene to a cold dichloromethane solution. Anal. Calcd: C, 53.2; H, 3.9; N, 1.6. Found: C, 52.9; H, 4.1; N, 1.6. μ_{eff}, 1.8 μ_B, ν_{CN}, 2170 cm^{-1} (s). It gave nonconducting solutions in acetonitrile and in dichloromethane.[8] The structure of the orange complex was confirmed by synthesis from $ReCl_3(MeCN)(PPh_3)_2$ and methyl isocyanide. Its synthesis from *trans*-$ReOCl_3(PPh_3)_2$ is a new example of a known reaction in which *trans*-$ReOCl_3(PPh_3)_2$ yields an octahedral complex of the type $ReCl_3L_n(PPh_3)_{3-n}$ (n = 1–3) when it is heated with a monodentate ligand (L) in the presence of a mild reducing agent which can form an oxide (e.g., triphenylphosphine).[9] In this case, methyl isocyanide can function both as the ligand (L) and as the reducing agent but the oxide, methyl isocyanate, is very reactive and was not detected among the products. When methyl isocyanide was added in a single batch instead of dropwise the yield of $ReCl_3(MeNC)(PPh_3)_2$ never exceeded 50% and the seven-coordinate complexes $ReCl_3(MeNC)_3(PPh_3)$ and $[ReCl_2(MeNC)_4PPh_3]PF_6$ were isolated from the mother liquors.[10]

A suspension of $ReCl_3(MeNC)(PPh_3)_2$ (3 3 mmol) and bis(diphenylphosphino)ethane (dppe, 7.1 mmol) in benzene (250 ml) was heated to reflux for 1.5 h under nitrogen and the solid product was recrystallized from dichloromethane–benzene to give dark green crystals of $ReCl_3(MeNC)(dppe)\cdot \frac{1}{3}C_6H_6$ in 98% yield. Anal. Calcd: C, 47.5; H, 3.9; N, 1.8. Found: C, 47.5; H, 4.0; N, 1.8. The solvent of crystallization was lost at 138 °C in vacuo to give $ReCl_3(MeNC)(dppe)$. Anal. Calcd: C, 45.9; H, 3.7; N, 1.9. Found: C, 46.3; H, 3.7; N, 1.8. μ_{eff}, 1.91 μ_B; ν_{CN}, 2150 cm^{-1} (s).

A suspension of $ReCl_3(MeNC)(dppe)\cdot \frac{1}{3}C_6H_6$ (3.2 mmol) and dppe (7.1 mmol) in moist methanol (i.e., methanol containing 0.02–1% water; 100 ml) was heated to reflux under nitrogen for 20 min. The resulting wine-red solution was concentrated to 20 ml and treated with sodium perchlorate to give a pink precipitate. This was washed with methanol and ether and recrystallized from dichloromethane–methanol to give pink prisms whose properties are consistent with the formulation $[ReCl(CONHMe)(dppe)_2]ClO_4$ (95% yield). Anal. Calcd: C, 55.2; H, 4.5; N, 1.2; Cl, 6.0. Found: C, 55.3; H, 4.4; N, 1.2; Cl, 5.8. μ_{eff}, 0.31 μ_B; Λ_0, 115 S cm^2 mol^{-1} in acetonitrile corresponding to a 1:1 electrolyte. The $\nu_{C=O}$ frequency of the amidic carbonyl occurred at 1580 cm^{-1} (ms) but the ν_{N-H} frequency was obscured by hydrogen bonding to ClO_4^-. It appeared clearly at 3305 cm^{-1} (m) in the purple tetraphenylborate which was obtained by metathesis. Anal. Calcd: C, 67.1; H, 5.2; N, 1.0. Found: C, 67.5; H, 5.1; N, 1.2. The NMR spectrum of the perchlorate in chloroform-*d* consisted of a multiplet at τ 2.75 (40 H, $8C_6H_5$), a broad signal at τ 5.2 (1 H, NH), a multiplet at τ 7.28 (8 H, $2\text{-}CH_2CH_2\text{-}$), and a doublet at τ 8.61 (3 H, $CH_3NH\text{-}$; J = 10 Hz) which spin decoupled on irradiation at τ 5.2. The doublet also collapsed to a sharp singlet on addition of deuterium oxide with disappearance of the signal at τ 5.2. The carbamoyl moiety is presumably formed by nucleophilic attack of coordinated isocyanide by hydroxide ion[11] in the intermediate $[ReCl(MeNC)(dppe)_2]^{2+}$.

The complex $[ReCl(CONHMe)(dppe)_2]ClO_4$ (**6**) reacted with bases in methanol to give **5** which separated almost quantitatively in lemon-yellow, diamagnetic crystals. In a typical experiment, **6** (2.0 g) in methanol (125 ml) was titrated with methanolic triethylamine under nitrogen until the red color of the solution was discharged. A pale yellow precipitate formed almost immediately and was filtered off after stirring the suspension at 0 °C for 1 h. It was recrystallized from dichloromethane–methanol to give **5** in 90% yield. Anal. Calcd: C, 60.3; H, 4.8; N, 1.3. Found: C, 60.6; H, 4.8; N, 1.2. We formulate **5** as a complex of methyl isocyanate, bonded through both carbon and nitrogen, on the following grounds: Its stoichiometry corresponds to the loss of the elements of $HClO_4$ by **6** and its gives nonconducting solutions; it is reprotonated by acetic of trifluoroacetic acid to give the cation of **6**; the doublet in **6** at τ 8.61 is replaced in **5** by a singlet at τ 7.81, with a chemical shift intermediate between the shifts observed for $CH_3NC\text{-}$ (τ 6.0–7.2) and $CH_3NHCO\text{-}$ (τ 8.1–8.7) in a series of diamagnetic complexes of Re^{III} and Re^{I}; $\nu_{C=O}$ in **6** at 1580 cm^{-1} is replaced in **5** by a strong and rather broad band at 1835 cm^{-1}, 435 cm^{-1} lower than in free methyl isocyanate but close to the $\nu_{C=O}$ frequency in penicillin (1779 cm^{-1}), β-propionolactone (1841 cm^{-1}), $Mn(C_5H_5)(Ph_2CCO)(CO)_2$ (1787 cm^{-1}),[1] and $Ni(CO_2)(PCy_3)_2$ (Cy = cyclohexyl; 1740 cm^{-1});[2] Jetz and Angelici[12] have shown that $W(C_5H_5)(CONHMe)(CO)_3$ reacts reversibly with triethylamine to give $[W(C_5H_5)(CO)_3]^-$ and free methyl isocyanate. Furthermore, **5** is reduced by carbon monoxide to $[Re(CO)(MeNC)(dppe)_2]^+$ ($\nu_{C=O}$, 1890 cm^{-1}; ν_{CN}, 2155 cm^{-1}), a reaction which would not be given by a hypothetical isomer of **5** containing adjacent carbonyl and methylnitrene groups. The product was isolated in 48% yield as the perchlorate. Anal. Calcd: 57.4; H, 4.5; N, 1.2. Found: C, 58.2; H, 4.6; N, 1.2.

The synthesis of complexes of organic isocyanates from the free ligands is hampered both by the high reactivity of organic isocyanates in the presence of metal ions and by their very weak coordinating ability. By contrast, organic isocyanides are the most powerful known neutral monodentate ligands, at least towards metals of d^8 configuration.[13] The coexistence of the labile complex $IrCl(N_2)(PPh_3)_2$ and phenyl isocyanate in dry chloroform,[3] and of **5** and methyl isocyanide in dichloro-

methane, therefore suggests that the stability of **5** towards loss of isocyanate is kinetic. In *methanol*, **5** reacts with methyl isocyanide to give $[Re(MeNC)_2(dppe)_2]^+$ (ν_{CN}, 2080 cm^{-1}). Anal. Calcd: C, 57.8; H, 4.7; N, 2.4. Found: C, 57.5; H, 4.7; N, 2.9.

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References and Notes

(1) W. A. Herrman, *Angew. Chem., Int. Ed. Engl.*, **13**, 335 (1974).
(2) M. Aresta, C. F. Nobile, V. G. Albano, E. Floriani, and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 636 (1975).
(3) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Am. Chem. Soc.*, **90**, 5430 (1968).
(4) G. La Monica, S. Cenini, and M. Freni, *J. Organomet. Chem.*, **76** 355 (1974).
(5) S. Hasegawa, K. Itoh, and Y. Ishii, *Inorg. Chem.*, **13**, 2675 (1974).
(6) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1767 (1970).
(7) M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. A*, 865, 2037 (1967).
(8) All ir spectra were measured in Nujol mulls and conductivities and magnetic moments were measured at room temperature.
(9) G. Rouschias, *Chem. Rev.*, **74**, 531 (1974), and references therein.
(10) Both of these compounds were identified by elemental analyses, Ir, NMR, and conductivity measurements. Whereas octahedral complexes of rhenium(III) usually exhibit T.I.P. equivalent to 1.5–2.1 μ_B at room temperature (ref 9) the two seven-coordinate complexes are diamagnetic. We have noticed that *all other seven-coordinate complexes of rhenium(III) whose susceptibilities have been recorded are also reported to be diamagnetic.*
(11) K. J. Knebel and P. M. Treichel, *Chem. Commun.*, 516 (1971); *Inorg. Chem.*, **11**, 1285 (1972).
(12) W. Jetz and R. J. Angelici, *J. Am. Chem. Soc.*, **94**, 3799 (1972).
(13) W. M. Bedford and G. Rouschias, *J. Chem. Soc., Dalton Trans.*, 2531 (1974); G. Rouschias and B. L. Shaw, *J. Chem. Soc.*, 2097 (1971).

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Book Reviews

Chemistry and Biochemistry of Amino Acids, Peptides and Proteins. Volumes 1–3 Edited by BORIS WEINSTEIN (University of Washington). Marcel Dekker, New York, N.Y. 1971. 1974. Vol. 1: x + 174 pp, $23.50. Vol. 2: xi + 380 pp, $23.50. Vol. 3: xi + 324 pp, $27.50.

These are the first three volumes of a series intended to appear more or less annually. Three to five reviews are contained per volume. The scope is broader than that of *Advances in Protein Chemistry*, since it covers the whole field of amino acids and of biomolecules in which the peptide group is important as well as significant aspects of related organic chemistry.

The topics are generally highly specialized (e.g., gramicidin, isoxazolium salt synthesis of peptides, cycloserine, HF in peptide chemistry, optical analysis of amino acid derivatives by gas chromatography). In itself this is neither good nor bad; each reader will find chapters of interest, some too narrow and some very useful because of the abundant detail possible for restricted subjects. The most specialized chapters generally contain much description of experimental methods. This will be of value to a researcher planning the use of a technique new to him or her. The chapter on ACTH-active peptides gives a long section (60% of the total) on details of the chemistry and strategy of specific syntheses. The general reader is not likely to want this. The intending synthesizer would be well served by a summary and a list of references, which he will wish to consult anyway. The second major section of this review, on structure–function relations, is of general interest. In Volume 2 (to a lesser extent Volume 3) a certain haste of preparation is noticeable in typographical errors, missing lines, and cloudy text. One chapter is especially difficult to read with numerous confusing sentences. (This may be connected with the fact that Volume 2 was not published on schedule.) Otherwise this review is well-filled with an abundance of valuable data which would be arduous to gather.

V. J. Hruby has provided an extensive review of studies of conformations of peptides in solution, mainly of NMR with comparisons of results by other methods. This review is aimed at the biochemist relatively unversed in NMR, giving generally the conclusions drawn about conformation, rather than detailed interpretation of the spectra. In some cases, oxytocin and vasopressin, for example, extensive discussion of the NMR data is given with more NMR detail than for most peptides. The literature cited is immense, 617 references to 1972, with an addendum of 161 references (not discussed in the text) through 1973, including for the latter, the titles of the papers.

The chapter (by Scannel and Pruess) on naturally occurring amino acid and peptide antimetabolites discusses briefly the detection and general mechanisms of antimetabolite action; most of this chapter is a catalog listing the structure of the antimetabolite, its reversants, source, mechanism, and, in some cases, stereochemistry, resolution, a reference to structure determination, or a review.

D. G. Brown's chapter on dioxygenases provides an overview of the organic chemistry of dioxygenase reactions, related nonenzymic reactions, and studies on the active sites of the enzymes. The summary deals with some directions of future research on mechanisms. Other reviews of general interest are on peptide alkaloids, γ-glutamyl peptides, and prebiotic syntheses.

The literature references are generally up to about 2 years (in some cases 3 years) prior to the date of publication.

This should be a useful series. Some topics will be of only modest interest to many, but a perusal will often be rewarding, and most readers will find reviews of much value.

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Chemisorption and Magnetization. By P. W. SELWOOD (University of California, Santa Barbara). Academic Press, New York, N.Y. 1975. ix + 172 pp. $19.50.

This book is an extensive revision of a previous monograph on this subject, Adsorption and Collective Paramagnetism, published by Professor Selwood in 1962. Although a good deal of the material in the present book was contained in the earlier monograph, revisions and expansions in the present volume have changed its emphasis significantly. The use of magnetic methods of particle size determination in commercial catalysts and for the determination of surface bond number for a variety of adsorbates is the principal concern of this work.

The book contains brief introductory chapters describing the concept of chemisorption and quickly reviewing the pertinent theory of magnetism and its application to small particles of ferromagnetic material. The discussion of other experimental surface chemistry techniques has been left out of the present volume, perhaps because of the greater familiarity with these techniques of the present-day surface scientist. The discussion of experimental techniques for the study of chemisorption by magnetic methods is very complete and, along with the references contained in these chapters, should give experimenters new to this field an excellent background for performing measurements of this kind.

The remainder of the book is devoted to a systematic presentation of the available data for adsorption on nickel, and to a lesser extent cobalt and iron, as obtained by magnetic methods. At several points in this presentation, isolated comparisons are made and connections suggested between the magnetic data obtained on commercial catalysts and the results of "clean surface" experiments with analogous systems. In this author's opinion, more discussion could have been devoted to these connections and comparisons, in particular, for the