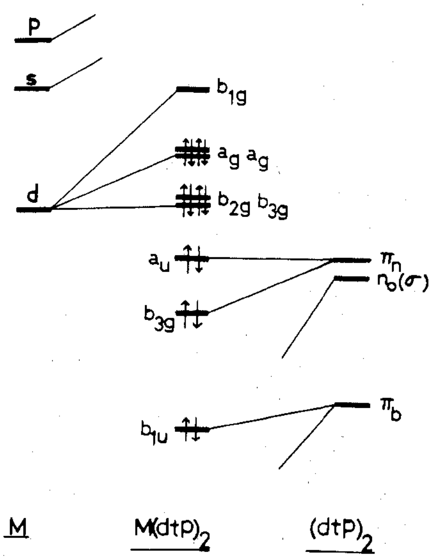

Figure 2. Qualitative MO scheme for M(dtp)$_2$ accounting for the first five PE bands.

compounds, like the M(dtp)$_2$ series, it is likely[6,34] that deviations from Koopmans' theorem are similar so that changes in orbital energies inferred from the PE spectra should be valid.

Figure 1 shows that Ni(dtp)$_2$ and Pt(dtp)$_2$ have very similar PE spectra, and it is convenient to discuss these first. In Ni(dtp)$_2$ the two d-orbital bands have equal areas, suggesting the splitting scheme shown in Figure 2. The d–d separation is 1.1 eV and compares with a splitting of approximately 1.3 eV proposed by Tomlinson and Furlani,[17] based on an analysis of the electronic spectrum. In Pt(dtp)$_2$ the two d-orbital bands again have equal area and the splitting is 1.2 eV. Both PE spectra have the third band at 9.2 eV which we assign to the nonbonding π orbital of a_u symmetry, which occurs at 9.1 eV in Hdtp. The a_u orbital is prevented by symmetry from mixing with any of the metal orbitals. The next two bands in the PE spectra of Ni(dtp)$_2$ and Pt(dtp)$_2$ are assigned to the b_{3g} (π_n) orbital lowered from 9.1 eV in Hdtp by interaction with the metal b_{3g} orbital and the b_{1u} (π_b) orbital shifted from 10.2 eV in Hdtp. We place the oxygen lone-pair IE's at $\gtrsim$10.8 eV, as in Hdtp.

The PE spectrum of Pd(dtp)$_2$ differs markedly from the others. The major differences are (1) the absence of the π_n IE at about 9.2 eV as seen in Ni(dtp)$_2$ and Pt(dtp)$_2$ and (2) the area ratio of the first two bands, which is about 1:1.8 for Pd(dtp)$_2$. We believe the most likely explanation of these facts is that the π_n (a_u) IE occurs within the second PE band. This accounts for its absence at 9.2 eV and the area ratio exceeding 1:1. The second PE band for Pd(dtp)$_2$ has a shoulder at 8.5 eV and a maximum at 8.7 eV. The 8.5-eV shoulder may be the a_u orbital or may result from d-orbital splitting. We do not attempt a distinction in Table I.

In planar d^8 systems it is usually found[11-16] that the M → L (π^*) charge-transfer transitions in the electronic spectrum follow the order Ni < Pd > Pt while the L(π) → M transitions have the order Ni > Pd < Pt. For all three metals the L(π) → L(π^*) transitions, where seen, occur at about the same energy. This suggests that the d–π_n separation in the M(dtp)$_2$ series should be least for Pd, in accord with our results. The only unanticipated result in our work is the small d-orbital separation found for Pd(dtp)$_2$.

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Registry No. Ni(dtp)$_2$, 16743-23-0; Pd(dtp)$_2$, 21312-72-1; Pt(dtp)$_2$, 37583-01-0; Hdtp, 298-06-6.

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Decarbonylation of β-Carbomethoxypropionylpentacarbonylmanganese(I)

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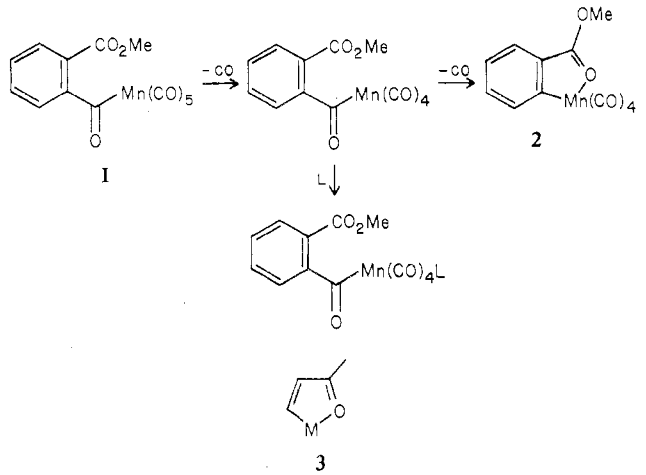
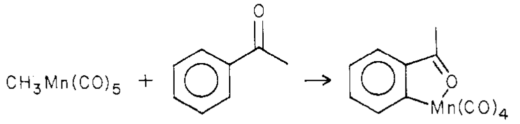
We recently reported the bisdecarbonylation of *o*-carbomethoxybenzoylpentacarbonylmanganese(I), **1**, to give **2** in which the carbomethoxy group acts as a chelating ligand.[1] A monodecarbonylated compound could be trapped with external phosphite but could not be directly observed by spectral means. The more rapid loss of the second CO from **1** might be related to the formation of a particularly stable chelated product (Scheme I).

β-Metallo-*α*,*β*-unsaturated carbonyl compounds with a chelating carbonyl group, **3**, are readily formed in many diverse

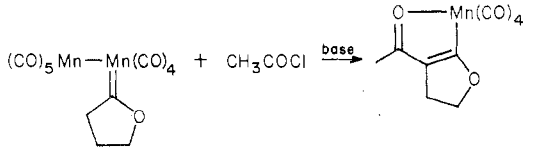
Scheme I



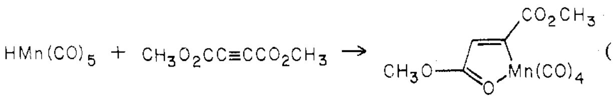
reactions (eq 1,[2] 2,[3] 3[4]) and appear to be especially stable. In



(1)

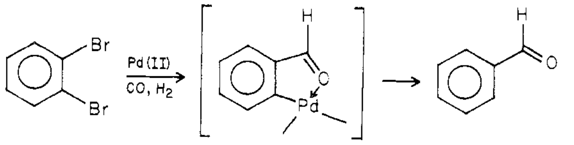


(2)

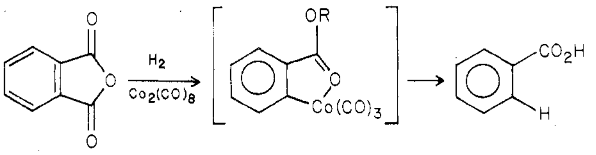


(3)

addition, the tendency to form such favorable intermediates apparently determines the course of reactions 4[5] and 5.[6]



(4)



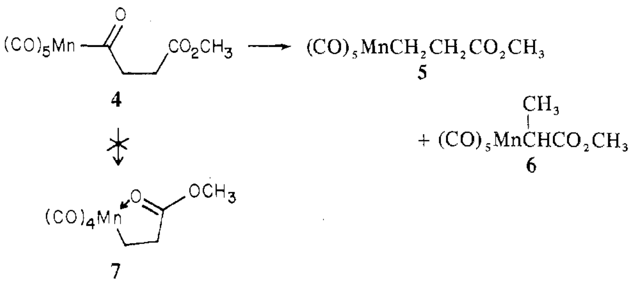
(5)

The ease of formation of compounds possessing structural unit **3** could be due to the stability of the five-member chelate ring and/or to electronic stabilization of the cyclic π-electron system. In an effort to separate and distinguish between these effects, we have studied the decarbonylation of β-carbomethoxypropionylpentacarbonylmanganese(I), **4**, which can form a five-member chelate but not a cyclic π-electron system.

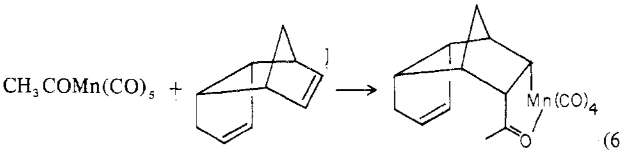
The decarbonylation of **4** occurs above its melting point (58–59 °C). When the reaction was carried out at 90 °C for 45 min, a mixture containing 71% **5** and 2% **6** in addition to 14% recovered **4** was obtained. No evidence for formation of decarbonylated chelate **7** was obtained. (See Scheme II.) The carbonyl stretch at 1744 cm^{-1} in **5** indicates that the ester group is not coordinated to manganese.

Decarbonylation of **4** also occurred at 75 °C in benzene. The ratio of **6**:**5** increased with time indicating that **5** was rearranging to **6** under the reaction conditions. Photolysis of **4** in hexane also gave mixtures of **5** and **6**. When CO was bubbled through solutions of **5** at room temperature in the dark, **4** was re-formed; the half-life for this recarbonylation of **5** to **4** was about 30 min.

Scheme II



The fact that **4** resists formation of ester-chelated **7** indicates that the special stability of structural unit **3** is due either to electronic stabilization or to the cis carbon–carbon double bond which holds the ester function in a conformation favorable for chelation. The recent report of Booth, Gardner, and Haszeldine[8] that stable chelates of β-keto manganese compounds form readily when the metal and the ketone functions are held in proximity by a bicyclo[2.2.1]heptane unit (see eq 6) provides evidence that stable chelates can be formed even



(6)

when electronic stabilization by a cyclic π-electron system is unavailable. Thus, the more rapid loss of the second CO from **1** is most likely associated with the formation of a conformationally preferred chelate and not with electronic stabilization of **2**.

The rearrangement of **5** to **6** probably occurs via a metal hydride addition–elimination mechanism. This rearrangement appears to be related to the rearrangement of β-keto iron compounds to α-keto iron compounds recently reported by Cooke.[9]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 267 infrared spectrophotometer. NMR spectra were taken using a JEOLCO MH-100 spectrometer. Mass spectra were taken using an AEI 902 mass spectrometer. Preparative thin-layer chromatography (TLC) was performed on Merck PF_{254} silica gel. All reactions were carried out under a nitrogen atmosphere. Hexane was stirred over H_2SO_4 and then distilled prior to use.

β-Carbomethoxypropionylpentacarbonylmanganese(I), 4, was prepared according to the method of Kraihanzel[7] in 87% yield and obtained as white needles: mp 57–58 °C (lit.[7] mp 57–58 °C); NMR ($CDCl_3$) δ 2.44 (t, J = 7 Hz, 2 H), 3.20 (t, J = 7 Hz, 2 H), 3.66 (s, 3 H, OCH_3); ir (hexane) ν_{CO} 2117 (w), 2058 (w), 2018 (s), 2006 (s, sh) cm^{-1}, C=O of ester at 1748 cm^{-1}, C=O of MnC=O at 1652 cm^{-1}; exact mass of $P - 2CO$ peak 253.9620 (calcd for $C_8H_7O_6Mn$ 253.9623).

Decarbonylation of 4. The pyrolysis of neat **4** (398 mg, 1.28 mmol) at 88–92 °C was carried out on a vacuum line (10^{-5} mm) for 45 min. After preparative TLC (9:1 hexane–Et_2O) a mixture of three compounds was separated and identified as **4** (56 mg, 14%, R_f 0.08), **5** (255 mg, 71%, R_f 0.27), and **6** (6 mg, 2%, R_f 0.17). Decarbonylation of **4** (300 mg, 0.97 mmol) was also accomplished by heating to 75 °C in 4 ml of benzene for 5 h. Preparative TLC gave **4** (71 mg, 24%), **5** (113 mg, 41%), and **6** (31 mg, 11%). Photolysis of **4** (150 mg, 0.485 mmol) at 350 nm in a Rayonet Srinivasan–Griffin photochemical reactor for 1.5 h in 5 ml of hexane gave after preparative TLC **4** (44 mg, 29%), **5** (51 mg, 37%), and **6** (3 mg, 2%).

Compound **5** was obtained as a white solid: mp 60–65 °C; NMR

($CDCl_3$) δ 1.22 (t, J = 7.5 Hz, 2 H, CH_2Mn), 2.68 (t, J = 7.5 Hz, 2 H, $CH_2C{=}O$), 3.68 (s, 3 H, OCH_3); ir (hexane) ν_{CO} 2110 (w), 2046 (w), 2014 (s), 1996 (s) cm^{-1}; C=O of ester at 1744 cm^{-1}; exact mass for P − 2CO peak 225.9677 (calcd for $C_7H_7O_5Mn$ 225.9674).

Compound **6** was obtained as a colorless oil: NMR ($CDCl_3$) δ 1.58 (d, J = 7.5 Hz, 3 H, CH_3), 2.31 (quartet, J = 7.5 Hz, 1 H, CH–Mn), 3.65 (s, 3 H, OCH_3); ir (hexane) ν_{CO} 2115 (w), 2054 (w), 2027 (s), 1999 (s) cm^{-1}; C=O of ester at 1711 cm^{-1}; exact mass of P − 1CO peak 253.9613 (calcd for $C_8H_7O_6Mn$ 253.9623).

Registry No. **4**, 21910-29-2; **5**, 59301-76-7; **6**, 59301-77-8.

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Matrix Isolation Study of the Products of Volatilization of Polymeric Sulfur Nitride

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Polymeric sulfur nitride has recently become a subject of great interest because of the demonstration of its metallic and superconducting properties.[1-6] Among the chemical and structural features of this material,[7,8] an unusual property for a polymeric substance is that it can be sublimed and in fact high-quality films of $(SN)_x$ have been prepared by sublimation of the polymer.[4] In an effort to shed some light on the depolymerization and repolymerization processes which occur in the sublimation, we have explored the matrix isolation technique as a means of characterizing, perhaps identifying, the molecular species in the vapor phase. This is a first report of that study.

Samples of the $(SN)_x$ polymer, prepared by Professor A. G. MacDiarmid and his co-workers,[8] were introduced into a Pyrex Knudsen cell which had been incorporated into an Air Products Displex refrigeration system. The polymer was heated to about 160 °C and the effluent from the cell orifice directed at a cold (10 K) window or surface about 1 in. away. At the same time a stream of argon gas was also directed at the cold surface, and during the matrix deposition process, the pressure in the refrigerator system was kept by pumping at about 10^{-4} Torr. The concentrations of our matrices are expressed by the M/A ratio where M is the number of moles of argon admitted to the cell and A is the amount of sulfur nitride arbitrarily expressed as the equivalent moles of $(SN)_4$. For purposes of reference, the infrared and uv–visible absorption spectra were determined for argon matrix isolated samples of pure S_2N_2 and of pure S_4N_4, two well-characterized sulfur nitride molecules.[9] The matrices containing either S_2N_2 or S_4N_4 molecules were all colorless.

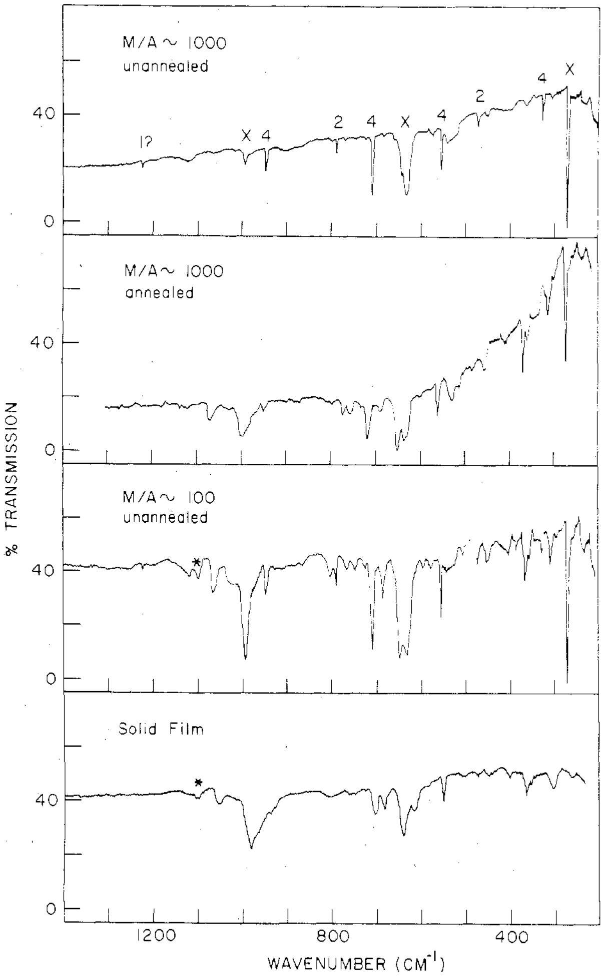

Figure 1. Infrared absorption spectra recorded at 10 K of condensed vapor species obtained by heating $(SN)_x$ to about 160 °C. The top three panels are argon matrices with the M/A ratios as indicated, each matrix deposited at the rate of about 0.01 mol of argon/h: top panel, freshly deposited matrix with $A = 10^{-5}$ molar equiv of $(SN)_4$; second panel, same matrix as above after being heated to 40 K for $^1/_2$ h; third panel, freshly deposited matrix with $A = 2 \times 10^{-5}$ molar equiv of $(SN)_4$; bottom panel, 20 μ thick solid film of condensed vapor species. Asterisk indicates impurity on window. The 1, 2, 4, and X signify SN, S_2N_2, S_4N_4, and unknowns.

Figure 1 shows the infrared spectrum of the vapor species obtained by heating $(SN)_x$ and then trapped in an argon matrix at an M/A ratio of about 1000. At this concentration the matrix is light orange. The infrared spectrum has a number of sharp absorption features and several broad ones. It is clear from the frequency coincidences and the relative intensities that most of the bands belong to S_2N_2 and S_4N_4. The very weak band at 1225 cm^{-1} suggests the presence also of a little SN (the vibrational frequency of the gaseous SN molecule[10] is given as 1204.1 cm^{-1}). Besides several weak features in the spectrum, the broader absorption maximum at 996 cm^{-1}, the one at 634 cm^{-1} with its two sharp shoulder peaks at 646.4 and 644.7 cm^{-1}, and the relatively sharp band at 273.2 cm^{-1} and its shoulders at 274.3 and 272.0 cm^{-1} are assigned to some unidentified species X, which is probably also responsible for the color of the matrix. Essentially the same spectrum is obtained even if M/A is increased to 10 000. When the matrix just described was annealed it acquired a rusty orange color and exhibited the infrared spectrum shown in Figure 1. The spectrum is now richer and the bands attributed to the X species are more intense relative to the S_2N_2 and S_4N_4 absorptions. From the intensity changes it is clear