stretch than for the Mo–O stretch. Thus the large shift of the 404-cm^{-1} band confirms its origin as the Mo–Mo stretch, whereas the metal-isotope shifts of the bands in the 300-cm^{-1} region are comparable to those found for Mo–O stretch in mononuclear molybdenum compound.[9]

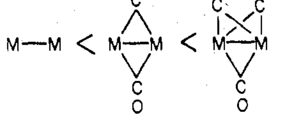
The 9-cm^{-1} shift of the Mo–Mo stretch is very close to that calculated for a Mo diatomic species, 8.7 cm^{-1}, where molybdenum masses are 92 and 96. If coupling of the Mo–Mo stretch with other coordinates were occurring, the size of the shift would be smaller. Therefore the present data provides direct evidence that the 404-cm^{-1} band represents a nearly pure Mo–Mo stretch, and this result favors the interpretation of Bratton, Cotton, Debau, and Walton, but because of sensitivity to experimental error the interpretation of Ketteringham et al. cannot definitely be ruled out. By contrast, the observed metal-isotope shift for $Fe_2(CO)_9$, 1.3 cm^{-1},[2] is much smaller than the value of 4.8 cm^{-1} calculated on the diatomic approximation for $^{54}Fe_2$ vs. $^{56}Fe_2$. To facilitate the comparison, we calculate the ratio of observed isotope shifts for $Mo_2(O_2CCH_3)_4$ to that of $Fe_2(CO)_9$, eq 1.

$$\frac{\nu[^{92}Mo_2(O_2CCH_3)_4] - \nu[^{NA}Mo_2(O_2CCH_3)_4]}{\nu[^{54}Fe_2(CO)_9] - \nu[^{56}Fe_2(CO)_9]} = \frac{9}{1.3} = 6.9 \tag{1}$$

It is well documented that the diatomic approximation is less satisfactory for the first transition series M–M-bonded compounds than for heavier metal analogues, because ligands which tend to ride with the metal exert a greater percentage effect on the lighter metals.[10] On the basis of complete vibrational analyses for other first-row carbonyls,[5] it is estimated that the effective mass change caused by the carbonyl ligands accounts for somewhat less than 1 cm^{-1} in the Fe–Fe isotopic shift. Accordingly, we increase the observed shift for the iron system by 1 cm^{-1} to account for the contributions from terminal CO ligands. With this correction the ratio given in eq 1 becomes 3.9. This mass-corrected shift ratio is to be compared to the theoretical ratio of shifts calculated on a diatomic approximation, eq 2.

$$\frac{\nu(^{92}Mo_2) - \nu(^{96}Mo_2)}{\nu(^{54}Fe_2) - \nu(^{56}Fe_2)} = \frac{8.7}{4.8} = 1.8 \tag{2}$$

The disparity between the mass-corrected isotopic frequency shift ratio and that calculated on the diatomic approximation resides in the fact that even after mass correction, the shift for $Fe_2(CO)_9$ is far less than that expected on a diatomic model. Apparently the internal displacement coordinates associated with the metal-bridging ligand system contribute far more to the M–M restoring force for $Fe_2(CO)_9$ than for $Mo_2(O_2CCH_3)_4$. One obvious origin of this difference is the geometry of the C-atom bridge in $Fe_2(CO)_9$ which directs a significant component of Fe–C stretch along the Fe–Fe axis. By contrast, the three-atom bridge in $Mo_2(O_2CCH_3)_4$ should be much more compliant. Additional evidence for the influence of CO bridges is available from the observed trends in M–M stretching frequencies for first-row single-bonded carbonyls which follow the order:[5]



Acknowledgment. Research performed at Abilene Christian University was supported by Robert A. Welch Foundation Grant No. R-483. The work performed at Northwestern University was supported by NSF Grant CHE 77-18747 A01, a NATO Fellowship to Y.M., and a NATO grant to D.F.S. Raman spectra were collected in the Optical Facility of the Northwestern University Materials Research Center which is partially supported by the NSF MRL program (Grant DMR 76-80847).

Registry No. $^{NA}Mo_2(O_2CCH_3)_4$, 14221-06-8; $^{92}Mo_2(O_2CCH_3)_4$, 70046-80-9.

References and Notes

(1) (a) Abilene Christian University. (b) Northwestern University.
(2) C. B. Cooper, III, S. Onaka, D. F. Shriver, L. Daniels, R. L. Hance, B. Hutchinson, and R. Shipley, *Inorg. Chim. Acta*, **24**, L92 (1977).
(3) W. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).
(4) A. P. Ketteringham, C. Oldham, and C. J. Peacock, *J. Chem. Soc., Dalton Trans.*, 1640 (1976).
(5) D. F. Shriver and C. B. Cooper, III, "Advances in Infrared and Raman Spectroscopy", R. J. H. Clark and R. E. Hester, Eds., Heyden and Sons, in press.
(6) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(7) A. P. Hagen, T. S. Miller, D. L. Terrell, B. Hutchinson, and R. L. Hance, *Inorg. Chem.*, **17**, 1369 (1978).
(8) D. R. Greig, G. C. Joy III, and D. F. Shriver, *J. Chem. Phys.*, **67**, 3189 (1977).
(9) Dennis Beaver, Thesis, Abilene Christian University, Abilene, TX, 1973.
(10) T. G. Spiro, *Prog. Inorg. Chem.*, **11**, 1 (1970).

Contribution No. 5979 from the Gates and Crellin Laboratories
of Chemistry, California Institute of Technology,
Pasadena, California 91125, and Contribution from the
Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1W5

Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Some (η^5-Cyclopentadienyl)nitrosyl Complexes of the Group 6B Elements[1a]

Robert E. Botto,[1b] Brian W. S. Kolthammer,[1c] Peter Legzdins,*[1c] and John D. Roberts*[1b]

Received February 20, 1979

During the past few years there have been considerable advances in the detection of nitrogen-15 NMR signals at the natural-abundance level.[2] Consequently, it is reasonable to expect that ^{15}N NMR spectra can be obtained for transition-metal nitrosyl complexes. Furthermore, these spectra should provide detailed structural and electronic information about the nitrosyl species in much the same way that ^{13}C NMR spectra elucidate the properties of transition-metal carbonyl compounds.[3] We now report the results of the first ^{15}N NMR study of some organometallic nitrosyl complexes, namely, (η^5-cyclopentadienyl)nitrosyl derivatives of chromium, molybdenum, and tungsten, and we also compare the ^{15}N and ^{13}C chemical shifts exhibited by these compounds.

Experimental Section

All of the compounds studied were of reagent-grade purity. The $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ and $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, W) complexes[4] $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$[5] and $(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)$[6] were prepared by published methods, and their purity was checked by elemental analyses. The infrared spectra of the complexes were recorded on a Perkin-Elmer 457 spectrophotometer and calibrated with the 1601-cm^{-1} band of polystyrene film.

^1H and ^{13}C NMR spectra were obtained with Varian Associates T60 and CFT20 spectrometers, respectively. The latter instrument was operated under conditions of proton decoupling with a deuterium lock. No relaxation reagent was employed during the measurement of ^{13}C NMR chemical shifts relative to internal solvent. The ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from $(CH_3)_4Si$. ^{15}N NMR spectra were recorded at a frequency of 18.25 MHz with a Bruker WH-180 pulse spectrometer that has been

Table I. Spectral Properties of the Complexes

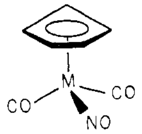
complex	ν(CO), cm^{-1} (in CH_2Cl_2)	ν(NO), cm^{-1} (in CH_2Cl_2)	$\delta(^1H)$, ppm (in $CDCl_3$)	$\delta(^{13}C)$, ppm (in $CDCl_3$)	$\delta(^{15}N)$, ppm (in $CHCl_3$)
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$	2020 s, 1945 s	1680 s	5.03	90.48 (cp) 237.05 (CO)	55.0
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$	2020 s, 1937 s	1663 s	5.53	93.24 (cp) 226.72 (CO)	43.6
$(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)$	1904 s	1607 s	5.13	93.25 (cp) 244.86 (CO)	41.4
$(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$	2010 s, 1925 s	1655 s	5.60	92.00 (cp) 217.17 (CO)	22.5
$(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$		1816 s, 1711 s	5.69	102.84	190.6
$(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$		1759 s, 1665 s	6.05	103.97	191.4
$(\eta^5\text{-}C_5H_5)W(NO)_2Cl$		1733 s, 1650 s	6.12	102.59	178.9
$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$		1667 s, 1512 m	5.17 (trans) 4.95 (cis)	101.35 (trans) 102.29 (cis)	127.7

described in detail elsewhere.[2] The ^{15}N NMR chemical shifts are reported in ppm downfield from 0.1 M 95% enriched $H^{15}NO_3$ in D_2O. The solutions contained about 2 g of complex in 20 mL of chloroform.

Results and Discussion

As expected, ^{15}N NMR signals at the natural-abundance level can indeed be detected for all eight nitrosyl complexes investigated. The observed ^{15}N NMR chemical shifts are tabulated in Table I, which also contains other pertinent spectral data for the compounds.

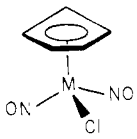
Each of the $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ complexes exhibits a single, sharp ^{15}N resonance attributable to its terminal nitrosyl ligand. These compounds are known to possess the "piano-stool" molecular structure, **1**, in the solid state.[7] These structures apparently also persist in solution as evidenced by the observation of just one ^{13}C resonance which arises from the two equivalent terminal CO groups present in each complex. Furthermore, there is an increase in carbonyl shielding as the metal is changed from Cr to Mo to W. A similar trend has been noted earlier for other isostructural carbonyl complexes of these metals,[3] and it has been suggested that the diamagnetic shielding influence of the metal itself is an important factor in producing this trend.[8] Consistent with this view, we observe an upfield shift of the nitrosyl ^{15}N resonances of the $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ complexes as the atomic weight of the group 6B metal increases.



1

Another trend in carbonyl shielding data, which has been reported previously, is that replacement of CO by better electron-donating ligands results in the remaining carbonyl ^{13}C resonances being situated at even lower field.[3] This feature is also evident in the ^{13}C NMR spectra of the related $(\eta^5\text{-}C_5H_5)Mo(CO)(L)(NO)$ (L = CO, PPh_3) complexes and can be rationalized in terms of increased metal-to-CO π back-bonding in the PPh_3 complex because of its lower ν(CO). However, the ^{15}N NMR spectra of the two complexes exhibit an exactly opposite trend in the nitrosyl ^{15}N resonances even though ν(NO) does decrease by 56 cm^{-1} upon substitution of CO by PPh_3. One possible explanation of these results is that whatever downfield effect is produced by increased metal-to-NO π back-bonding is more than canceled by changes in the second-order paramagnetic effect at the nitrogen. The ^1H and ^{13}C resonances observed for the cyclopentadienyl ring atoms in complexes of this type are relatively insensitive to such changes in the metal's coordination sphere and thus provide no obvious additional information. Interestingly, the ^{13}C and ^{15}N NMR spectra of $(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)$ do display $J_{^{31}P-^{13}C(O)}$ and $J_{^{31}P-^{15}N}$ coupling constants of 11.8 and 5.9 Hz, respectively, the latter being the first such constant to be reported.

The ^{15}N NMR spectra of all the $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ complexes we have studied exhibit just one resonance due to the two terminal nitrosyl ligands in each compound, thereby suggesting that they maintain the molecular structure **2** in solution.[9] Whereas δ (^{13}C) values of terminal carbonyls occur in a fairly narrow range,[10] the nitrosyls are markedly more deshielded in these complexes than in the dicarbonylnitrosyl species. In addition, there is no longer a regular increase in nitrosyl shielding as the metal is varied from Cr to W. Clearly, more ^{15}N NMR data must be obtained before the factors affecting ^{15}N chemical shifts can be fully understood. It should also be noted that the ^1H and ^{13}C resonances of the $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ complexes come at lower fields than the corresponding resonances of the $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ compounds.



2

The last complex studied, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, is known to exist in solution as an equilibrating mixture of cis and trans NO-bridged dimers, with polar solvents displacing the equilibrium in favor of the cis isomer.[11] Consequently, we observe that the ambient-temperature ^{13}C NMR spectrum of the complex in $CDCl_3$ consists of two resonances at δ 101.35 and 102.29 attributable to the nonequivalent sets of cyclopentadienyl carbon atoms. The intensities of these signals (~20:1) permit their assignment to the trans and cis forms, respectively, by comparison with the published ^1H NMR data.[11] In contrast, we find that the ^{15}N NMR spectrum of the dimer dissolved in $CHCl_3$, CH_2Cl_2, or acetone displays just one resonance, the respective δ values being 127.7, 128.5, and 127.4. This observation suggests that the nitrosyl ligands are undergoing rapid intramolecular rearrangement on the NMR time scale in both the cis and trans isomers.[12] The presence of one ^{15}N resonance indicates either fortuitous coincidence of the signals due to the two isomers or that the signal due to the cis isomer is too weak to be detectable under the experimental conditions employed, because cis–trans interconversion does not occur until ~90 °C.[11] To resolve this point and to clarify the mode of rearrangement of the complex, we have initiated a variable-temperature ^{15}N NMR study of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.

The addition of 10 mole % tris(acetylacetonato)chromium(III), $[Cr(acac)_3]$,[13] to $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in CH_2Cl_2 greatly shortens the ^{15}N relaxation times without causing contact shifts, $\delta(^{15}N)$ = 128.6, or line broadening by making $T_2 \ll T_1$. Samples containing the relaxing agent required only about one-tenth the accumulation time required for undoped samples to produce ^{15}N spectra having comparable signal-to-noise ratios.

Registry No. (η^5-C_5H_5)Cr(CO)$_2$(NO), 36312-04-6; (η^5-C_5H_5)Mo(CO)$_2$(NO), 12128-13-1; (η^5-C_5H_5)Mo(CO)(PPh$_3$)(NO), 32660-56-3; (η^5-C_5H_5)W(CO)$_2$(NO), 33114-09-9; (η^5-C_5H_5)Cr(NO)$_2$Cl, 12071-51-1; (η^5-C_5H_5)Mo(NO)$_2$Cl, 12305-00-9; (η^5-C_5H_5)W(NO)$_2$Cl, 53419-14-0; [(η^5-C_5H_5)Cr(NO)$_2$]$_2$, 36607-01-9.

References and Notes

(1) (a) Supported by the National Science Foundation and by the National Research Council of Canada. (b) California Institute of Technology. (c) The University of British Columbia.
(2) Gust, D.; Moon, R. B.; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4696–700.
(3) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1–25 and references cited therein.
(4) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126–31.
(5) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.*, **1979**, *19*, 208–12.
(6) Brunner, H. *J. Organomet. Chem.* **1969**, *16*, 119–24.
(7) Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P. E.; Alt, H. G. *J. Organomet. Chem.* **1979**, *165*, 65–78.
(8) Cronin, D. L.; Wilkinson, J. R.; Todd, L. J. *J. Magn. Reson.* **1975**, *17*, 353–61.
(9) Such a structure has been determined for the chromium complex in the solid state: Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1966**, 1095–103.
(10) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.
(11) Kirchner, R. M.; Marks, T. J.; Kristoff, J. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 6602–13.
(12) Cf. the bridge–terminal CO interchange mechanism of the isoelectronic [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ dimer: Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589–94.
(13) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456–7.

Contribution from the Departments of Chemistry,
William Marsh Rice University, Houston, Texas 77001,
and University of California, Berkeley, California 94720

Reactions of Main Group 4 Species with Organic Reagents. 1. Tin and Tin(II) Fluoride Reactions with Ethylene in Argon Matrices[2]

P. F. Meier,[1a] D. L. Perry,*[1b] R. H. Hauge,[1a]
and J. L. Margrave*[1a]

Received December 8, 1978

During the last several years, much attention has been focused on the reactions of metal vapors with a wide array of chemical species. The integration of the high-temperature volatilization (and subsequent condensation) of the reactive metal vapors and coreactants with the technique of matrix isolation spectroscopy has provided a convenient means of investigating possibly reactive intermediates in hetero- and homogeneous catalysis which are often transient species and thus difficult to observe. This approach has permitted such systems as carbon monoxide on metal surfaces, metal atom–olefin interactions, and the catalytic oxidation of ethylene to ethylene oxide to be studied, with many of these systems being quite elegantly and extensively investigated by Ozin and his co-workers.[3] By trapping and thus stabilizing these intermediates, one may then study them by means of a variety of techniques such as infrared, Raman, and ultraviolet–visible spectroscopy in order to more fully elucidate their bonding and spectroscopic properties. Matrix isolation experiments also allow researchers to study the feasibility of new reaction systems advancing to macroscale or production scale syntheses which involve much more costly expenditures in both production equipment and materials.

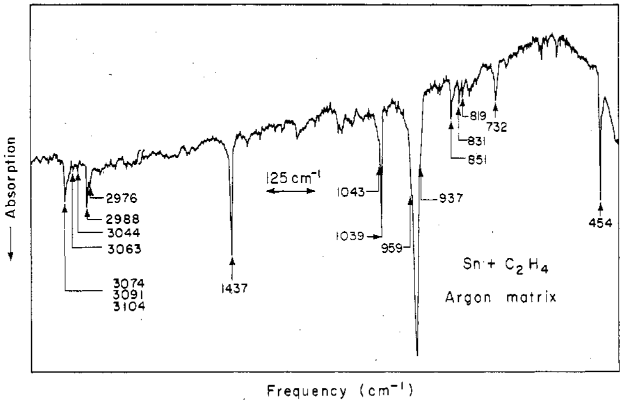


Figure 1. Infrared spectrum of the matrix-isolated product formed in the reaction of tin with ethylene.

Current interest in this laboratory in the utilization of matrix isolation spectroscopy to monitor and study chemical reactions lies in the continuation of ongoing research concerning the chemistry of main group 4 elements with added emphasis on the dipositive state, research which has already yielded a rich chemistry for divalent silicon.[4] Bassler et al., for example, first demonstrated the reactivity of certain fluorides (and trapping at rare-gas-matrix temperatures) by reporting the reactions of SiF_2 with small molecules such as CO and NO.[5] In addition, tin vapor has been found to react[6] with oxygen (which is isoelectronic with ethylene as reported in this study) to form molecular species of the types SnO_2 and Sn_2O_2. Both tin metal and tin(II) halides have also been shown to be quite important catalysts in several reactions of olefins,[7] ethylene being the simplest, prototypical example; the facile homogeneous hydrogenation of ethylene has been effected by use of Pt(II)/Sn(II) solutions containing tin–platinum clusters.[8]

The present report details the results of the matrix isolation infrared study of the reaction of tin and tin(II) fluoride with ethylene with the reaction products being trapped in argon matrices and represents the first evidence for a reaction chemistry involving the group 4A elements with olefins in the gas phase. Such data should be quite useful in providing initial insight into the use of tin and tin(II) species as catalysts in several industrially important reaction systems in which high-temperature complexes similar to the ones reported here quite likely exist and serve as reactive intermediates or metastable species for such catalytic processes; also, the initial data gathered here serve as the basis for further work relating to the vapor-phase synthesis of group 4A metal clusters with olefins as well as metal atom/organic reagent slurries which can serve as active, synthetic reagents themselves.

Experimental Section

The matrix isolation trapping apparatus used in this investigation has been described previously[9] with cooling of the copper deposition block being provided by an Air Products helium closed-cycle refrigeration system. Both tin metal and tin(II) fluoride were vaporized from a tantalum foil furnace at 1050 and 400 °C, respectively, and condensed into argon matrices; the furnace temperature was monitored by utilizing a standard Pt–Pt 10% Rh thermocouple. All spectra were recorded in the 400–4000-cm^{-1} range with a Beckman IR-9 spectrometer calibrated against water vapor. Trapping times for all cocondensation reactions reported here were 0.5 h unless otherwise stated.

Tin powder (Fisher), tin(II) fluoride (Alfa Ventron), and ethylene (Matheson. 99.99% purity) were used as received with no further purification. Impurities were monitored by running blank spectra of each reactant and, in the case of tin(II) fluoride and ethylene, by checking the spectra against published spectra.

Results and Discussion

Sn/C_2H_4 Reaction. Matrix isolation experiments in this laboratory have demonstrated the existence of a reaction when tin vapor and ethylene are cocondensed in an argon matrix,

0020-1669/79/1318-2051$01.00/0