Inorganica Chimica Acta, 26 (1978) 29–36
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Studies of Dinuclear Metal Carbonyl Carbenes. Synthesis, Characterization, and Raman Spectra of Amino- and Alkoxycarbenes*

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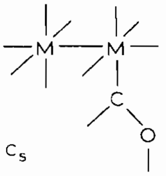
Received April 18, 1977

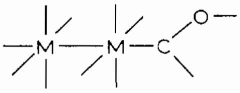
*The new dinuclear metal carbene complexes $(CO)_9Re_2C(OC_2H_5)R$ ($R = CH_3, C_6H_5$) and $(CO)_9M_2C(NHCH_3)CH_3$ (M = Mn, Re) have been synthesized. All products were obtained with the carbene in the equatorial position (*cis *to the M–M bond) and the methylaminomethyl carbene ligand in the* syn *configuration. The Re aminocarbene could be isomerized into a* syn–anti *mixture, but the* anti *form of the Mn aminocarbene could not be isolated. Low frequency Raman spectra for several dinuclear carbenes show an intense $\nu_{(M-M)}$ band near 120 cm^{-1} for M = Re and 150–160 cm^{-1} for M = Mn; the frequency of this band is relatively insensitive to substitution of carbene for carbonyl in the* cis *position and to changes in the* cis *carbene. The pattern of Raman bands in the rest of the $\Delta\nu$ = 100–650 cm^{-1} region confirms the structural similarity of the series of compounds studied.*

Introduction

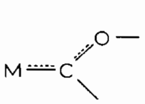
Transition metal carbene complexes, particularly the mononuclear carbonyls of Group VIB, have been studied quite extensively as evidenced by the presence of several review articles [1–5]. A few complexes containing two or more metal atoms have been reported. Fischer and his co-workers reported the synthesis and characterization of several dinuclear alkoxycarbenes of the type $(CO)_9M_2C(OR')R$ (M = Mn, Tc, Re; R = alkyl or aryl; R′ = alkyl) [6, 7]. The present work began after Fischer's first paper [6] when there was some uncertainty as to whether the carbene ligand was in the equatorial or the axial position (C_s or C_{4v} symmetry) relative to the Mn–Mn bond when the carbene was bulky. An X-ray crystal structure determination of $(CO)_9Mn_2C(OCH_3)C_6H_5$ subsequently showed that the carbene occupies the equatorial position (C_s) and is in the *syn* configuration in the solid state [8]. Similarly, Casey *et al.*, reported the mixed dinuclear complex $(CO)_5MnRe(CO)_4C(OCH_3)CH_3$ to have C_s symmetry. An X-ray study showed that the carbene ligand was in the *syn* configuration and was bonded to Re [9]. The other reported dinuclear manganese and rhenium alkoxycarbenes were found to have C_s symmetry based on their solution ir spectra [6, 7]. Nmr data indicated that for chromium alkoxycarbenes there was an equilibrium mixture of *syn* and *anti* configurations in solution, that the position of the equilibrium depended upon the solvent, and that the rate of rotation about the :C–O bond was temperature dependent [10].



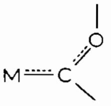
C_s



C_{4v}



SYN



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Klabunde reported the conversion of $(CO)_5CrC(OCH_3)CH_3$ to the corresponding aminocarbene by reaction with H_2NCH_3 [11] to give a product with the aminocarbene ligand in the *syn* configuration as shown by X-ray crystallography [12]. No one has reported the preparation and study of methylaminocarbenes of dinuclear metal carbonyl complexes.

The location of the aminocarbene ligand relative to the metal–metal bond (C_s or C_{4v} symmetry), its configuration (*syn* or *anti*), and its susceptibility

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*Presented in part at the 10th Great Lakes American Chemical Society Meeting (paper #211), June 17–19, 1976, Evanston, Illinois.

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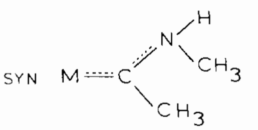

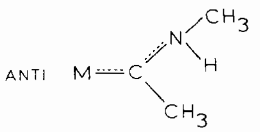

to *syn–anti* isomerization are of interest and are reported in this paper for the Re–Re and Mn–Mn carbonyls. We also report the synthesis and symmetry of two new alkoxycarbenes containing the Re–Re bond, and the Raman spectra of several of these dinuclear metal carbonyl carbenes in the low $\Delta\nu$ region where intense M–M stretching modes are observed.

Experimental

Equipment and General Techniques

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were purchased from Pressure Chemical Co., Pittsburgh, Pa. and sublimed before use.* Solutions of methyl- and phenyllithium were purchased from Ventron Alfa Products, Beverly, Mass., anhydrous monomethylamine from Matheson Gas Products, Lyndhurst, N.J., and silica gel (60–200 mesh) from Matheson Coleman & Bell, Norwood, Ohio. R_3OBF_4 ($R = CH_3, C_2H_5$) was prepared according to the literature [13]. Spectrophotometric grade solvents for ir and nmr and deuterated solvents for nmr (at least 99.5 atom %D) were purchased from several suppliers. All other solvents were dried before use by standard methods, such as refluxing over and distilling from $LiAlH_4$. All reactions were run under N_2 on the bench and all workup was done under N_2. All purification and sample preparation work was done in a VAC HE-43-2 dry box equipped with a HE-493 Dri Train from Vacuum Atmospheres Co., Hawthorne, Cal.

Melting points are uncorrected as obtained in sealed capillaries (N_2 atmosphere) using a Mel-Temp apparatus from Laboratory Devices, Cambridge, Mass. Ir spectra were recorded using a Perkin–Elmer 457 grating infrared spectrophotometer with a 0.10 mm KBr solution cell. Nmr spectra were obtained on a Hitachi Perkin–Elmer R20A spectrometer equipped with a variable temperature R-202VT controller and a proton spin decoupler R-201SD. Elemental analyses and molecular weights (osmometry in acetone) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Raman spectra were obtained on a Spex Industries Model 1401 Laser Raman Spectrophotometer equipped with a Coherent Radiation mixed gas argon–krypton ion laser and an argon ion laser. Power at the sample was generally between 50 and 100 milliwatts. It was sometimes necessary to filter the incident radiation with neutral density filters to avoid thermal or photolytic destruction of the sample. Spectra were obtained on solid samples in capillary tubes sealed under N_2 and were excited by 568.2, 514.5 and 488.0 nm laser frequencies. Results are reported only for samples which showed no visible evidence of decomposition, and which gave a reproducible spectrum over a period of several hours of exposure to the laser beam.

Syntheses

Quantities and results of representative runs are given below.

$(CO)_9Mn_2C(NHCH_3)CH_3$

Anhydrous H_2NCH_3 was bubbled through 1.19 mmol of $(CO)_9Mn_2C(OCH_3)CH_3$ in 20 ml ether for 15 min at room temperature with no color change. Vacuum evaporation of the solvent gave an orange solid that was eluted from a 10 × 2 cm silica column with toluene to give 0.35 g (69% yield) of orange $(CO)_9Mn_2C(NHCH_3)CH_3$ (m.p. 95 °C). *Anal.* Found: C, 34.32; H, 1.64; N, 3.26; O not available in presence of Mn. Mol. wt., 419. $C_{12}H_7NO_9Mn_2$ calcd.: C, 34.38; H, 1.68; N, 3.24%. Mol. wt., 414.

$(CO)_9Re_2C(NHCH_3)CH_3$

As for $(CO)_9Mn_2C(NHCH_3)CH_3$, H_2NCH_3 was reacted with 0.416 mmol of $(CO)_9Re_2C(OC_2H_5)CH_3$ to yield 0.215 g (76% yield) of cream colored $(CO)_9Re_2C(NHCH_3)CH_3$ (m.p. 123 °C) which was eluted from a 10 × 2 cm silica column with 75:25 toluene: hexane after first removing the $Re_2(CO)_{10}$ with 50:50 toluene:hexane. *Anal.* Found: C, 21.02; H, 1.00; N, 1.93; O, 21.26. Mol. wt., 678.
$C_{12}H_7NO_9Re_2$ calcd.: C, 21.14; H, 1.04; N, 2.05; O, 21.13%. Mol. wt., 682.

$(CO)_9Re_2C(OC_2H_5)CH_3$

An ether solution of CH_3Li (2.101 mmol) was added dropwise to 1.58 mmol of sublimed $Re_2(CO)_{10}$ in 150 ml of ether at 0 °C. Stirring was continued at 0 °C for 1 hour, giving a rust–orange solution. Aspirator evaporation left an oily dark solid which was dissolved in 15 to 20 ml of ice water (O_2 free). $(C_2H_5)_3OBF_4$ (1.58 mmol) was quickly added and the mixture extracted with several portions of pentane (about 300 ml total). The organic layers were combined, dried over Drierite for a few minutes, filtered, and evaporated with aspirator vacuum yielding an orange oil. The oil was chromatographed at least twice on a 20 × 2 cm silica gel column. Hexane eluted the product as a yellow band. Vacuum evaporation gave 0.528 g (48% yield) of yellow–orange $(CO)_9Re_2C(OC_2H_5)CH_3$ (m.p. 69 °C). *Anal.* Found: C, 22.17; H, 1.28; O, 23.05. Mol. wt., 701. $C_{13}H_8O_{10}Re_2$ calcd.: C, 22.41; H, 1.16; O, 22.97%. Mol. wt., 697.

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*We found extreme difficulty in synthesizing the carbenes from $Re_2(CO)_{10}$ obtained from a different supplier.

TABLE I. Carbonyl Stretching Frequencies (cm^{-1}).

$(CO)_9Re_2C{\genfrac{}{}{0pt}{}{/OC_2H_5}{\backslash CH_3}}$		$(CO)_9Re_2C{\genfrac{}{}{0pt}{}{/OC_2H_5}{\backslash C_6H_5}}$	$(CO)_9Re_2C{\genfrac{}{}{0pt}{}{/NHCH_3}{\backslash CH_3}}$		$(CO)_9Mn_2C{\genfrac{}{}{0pt}{}{/NHCH_3}{\backslash CH_3}}$	
Ir[a]	Raman[b]		Ir	Raman	Ir	Raman
2108 (m)[c]	2108 (m)	2104 (m)	2104 (m)	2100 (s)	2087 (m)	2033 (m)
2049 (s)	2035 (w)	2052 (s)	2041 (s)		2015 (vs)	2020 (m)
		2030 (m, sh)				
2021 (m)	2023 (w)	2025 (m)	2019 (m)	2028 (m)	2008 (s)	
		2010 (s, sh)				
2002 (vs)	2004 (w)	2003 (vs)	1994 (vs)	2003 (s)	1998 (vs)	1994 (m, sh)
1995 (vs)		1995(s)	1984 (s)	1991 (m, sh)	1976 (s)	1985 (s)
1975 (m)	1969 (w)	1977 (m)	1977 (s)		1970 (s)	1973 (w)
1959 (s)		1966 (m)	1967 (m)		1960 (m)	
		1960 (m, sh)				
1953 (s)	1950 (s)	1953 (s)	1945 (s)	1954 (s)	1946 (s)	
			1937 (m)	1934 (w)	1934 (w)	1940 (w)

[a] Ir spectra taken using a Perkin–Elmer 457, 0.100 mm hexane. [b] Raman spectra are for solids sealed under N_2 in glass capillary tubes. Raman spectrum not obtained for $(CO)_9Re_2C{\genfrac{}{}{0pt}{}{/OC_2H_5}{\backslash C_6H_5}}$ [c] w = weak, m = medium, s = strong, vs = very strong, sh = shoulder

TABLE II. *Syn* and *Anti* Isomers of $(CO)_xM_yC(NHCH_3)CH_3$.

	N–H Vibrational Frequencies[a]		
$(CO)_xM_y$	Isomer	N–H Stretch	N–H Bend
$(CO)_5Cr$[b]	*syn*	3400	1555, 1532
	anti	3330	1575
$(CO)_9Re_2$	*syn*	3400	1540 br
	anti	3330	1560
$(CO)_9Mn_2$	*syn*	3405	1545 br
	anti	–	–

[a] cm^{-1}; Nujol Mull; Perkin–Elmer 457; br = broad. [b] See ref. 14.

$(CO)_9Re_2C(OC_2H_5)C_6H_5$

Similarly to $(CO)_9Re_2C(OC_2H_5)CH_3$, 1.515 mmol of $Re_2(CO)_{10}$ was reacted with 3.030 mmol of C_6H_5Li. The yield was 0.482 g (42%) of orange $(CO)_9Re_2C(OC_2H_5)C_6H_5$ (m.p. 52–55 °C). *Anal.* Found: C, 29.74; H, 1.55; O, 22.40. Mol. wt., 750. $C_{18}H_{10}O_{10}Re_2$ calcd.: C, 28.50; H, 1.33; O, 21.09%. Mol. wt., 759.

Syn–Anti Isomerization

syn$(CO)_9Re_2C(NHCH_3)CH_3$

i) KOH in methanol: 1.6 mmol of KOH was added to 0.367 mmol of *syn*$(CO)_9Re_2C(NHCH_3)CH_3$ in 5 ml anhydrous CH_3OH and the solution was shaken until dissolution occurred. After 30 min at room temperature there was little apparent color change; 15 to 20 drops of water was added to quench the reaction and precipitate the product. The solid was washed twice with 1 ml aliquots of hexane and chromatographed on a silica column with toluene. Only unchanged starting material was recovered.

ii) Na in t-butyl alcohol: A solution of 0.0040 g (0.174 mmol) Na in 5 ml freshly dried t-butyl alcohol was added to 0.25 g (0.367 mmol) of solid *syn*$(CO)_9Re_2C(NHCH_3)CH_3$. The solution quickly turned bright yellow. After 30 min at room temperature about 10 ml water was added. The precipitated product (light yellow) was washed with hexane. Nmr spectra in $CDCl_3$ before and after column chromatography (9 X 2 cm silica, 50:50 toluene:hexane eluent) showed an isomeric mixture of 57% *syn*- and 43% *anti*$(CO)_9Re_2C(NHCH_3)CH_3$.

syn*$(CO)_9Mn_2C(NHCH_3)CH_3$*

KOH in methanol and Na in t-butyl alcohol: In a manner similar to that with *syn*$(CO)_9Re_2C(NHCH_3)CH_3$, *syn*$(CO)_9Mn_2C(NHCH_3)CH_3$ was treated with KOH in CH_3OH and Na in t-butyl alcohol. In each attempt a blood-red color developed quickly. Because precipitation was slow or difficult when H_2O was added, the mixture was extracted with ethyl ether (about 50 to 75 ml) after the H_2O addition. Upon vacuum evaporation of the ether layer a red–orange oil remained. Nmr spectra before silica chromatography had only very broad peaks. Solution ir spectra

TABLE III. *Syn* and *Anti* Isomers of $(CO)_xM_yC(NHCH_3)CH_3$. Chemical Shifts in $CDCl_3$[a]

	:C–CH$_3$		N–CH$_3$		N–H
	syn	*anti*	*syn*	*anti*	
$(CO)_5Cr$[b]	2.70 s ($J_{CH_3CH_3}$ ~ 0.3)		3.21 d (J_{HNCH_3} 5.1)		~8.35 br
		2.81 s ($J_{CH_3CH_3}$ 0.85)		3.65 d (J_{HNCH_3} 4.9)	~8.20 br
$(CO)_9Re_2$	2.69 s ($J_{CH_3CH_3}$ < 0.5)		3.09 d (J_{HNCH_3} 5.4)		~8.5 br
		2.90 s ($J_{CH_3CH_3}$ ~ 1)		3.36 d (J_{HNCH_3} 4.8)	~8.5 br
$(CO)_9Mn_2$	2.70 s ($J_{CH_3CH_3}$ < 0.5)	–	3.19 d (J_{NHCH_3} 5.0)	–	~8.9 br

[a] Ppm relative to TMS; s = singlet, d = doublet, br = broad; J in Hz. [b] See ref. 14.

(hexane) showed only $(CO)_9Mn_2C(NHCH_3)CH_3$, although some red material was insoluble in hexane. Silica chromatography (ether eluent) gave an orange solid that was shown by nmr to be pure *syn* isomer. A small layer of unidentified red material remained tightly bound at the top of the silica column.

Results and Discussion

Spectra Data for Syn*$(CO)_9M_2C(NHCH_3)CH_3$ and $(CO)_9Re_2C(OC_2H_5)R$ (M = Mn, Re; R = CH_3, C_6H_5)*

Solution infrared spectra (Table I) exhibited the pattern of nine peaks expected for the $(CO)_9M_2$-carbene compounds having C_s symmetry. These data indicate that not only are the alkoxycarbenes synthesized in the equatorial, or *cis*, position relative to the M–M bond, but also that when the alkoxycarbenes are converted to the methylaminomethylcarbenes the symmetry is unchanged. That is, by whatever mechanism the conversion takes place, it occurs with retention of symmetry (C_s), in high yields, and without M–M bond cleavage.

The observation of the N–H stretch at about 3400 cm^{-1} and the N–H bend at about 1545 cm^{-1} (Table II) in the solid phase ir spectra suggests that the $(CO)_9M_2C(NHCH_3)CH_3$ (M = Mn, Re) compounds are synthesized with the methylaminomethylcarbene in the *syn* configuration. The N–CH_3 chemical shifts (Table III) of the $(CO)_9M_2C(NHCH_3)CH_3$ (*M* = Mn, Re) of 3.19 and 3.09 δ, respectively, are quite close to the 3.21 δ value reported for N–CH_3 in *syn* $(CO)_5CrC(NHCH_3)CH_3$ and far from the 3.65 δ value reported for the corresponding *anti* isomer [14, 15]. Taken together these data leave little doubt that the methylaminomethylcarbene ligand is in the *syn* configuration in these dinuclear compounds, as they are synthesized from the alkoxycarbenes. Similarly Fischer found exclusive *syn* configuration in the methylaminomethylcarbene ligand when he synthesized the less sterically hindered mononuclear chromium and tungsten methylaminomethylcarbenes from the corresponding alkoxycarbenes [14, 15]. Thus, the presence of the M–M bond and the rather bulky $(CO)_5M$ moiety *cis* to the alkoxycarbene does not affect the symmetry of the compound nor the configuration of the ligand upon conversion to the methylaminomethylcarbene.

The existence of the M–M bond and the structural similarity of all dinuclear carbene complexes reported here is confirmed by the low and middle frequency Raman spectra. In each compound a very intense band is observed in the low $\Delta\nu$ region (near 120 cm^{-1} for M = Re and at 150–160 cm^{-1} for M = Mn). These bands are very near in frequency to the most intense low frequency bands of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ at 124 cm^{-1} and 164 cm^{-1}, respectively (see Table IV and Fig. 1). These bands in the $M_2(CO)_{10}$ species have been assigned to the metal-metal bond vibration which is expected to be very intense as a result of a resonance interaction with the $\sigma \rightarrow \sigma^*$ transition involving electrons largely localized in the M–M bond [16]. Two explanations may be given for the nearly constant ν(M–M) values for each series of compounds (the series of dinuclear Re compounds and of dinuclear Mn compounds). First, the substitution of a carbene ligand for a carbonyl in the *cis* position would be expected to have a smaller effect on the metal-metal bond strength than would *trans* substitution simply because *cis* ligands share fewer bonding orbitals than do *trans* ligands. Second, the equatorial ligands in dinuclear metal carbonyls make only a very small mass contribution in the kinetic energy of the mode with the largest metal-metal stretching

TABLE IV. Low Frequency Raman Spectra of $M_2(CO)_9$·Carbenes (M = Re, Mn)[a].

$Re_2(CO)_{10}$	$Re_2(CO)_9C(OC_2H_5)(CH_3)$	$Re_2(CO)_9C(OCH_3)(CH_3)$	$Re_2(CO)_9C(OC_2H_5)(C_6H_5)$	$Re_2(CO)_9C(NHCH_3)(CH_3)$
33 (m)[b]	39 (m)	31 (w)	39 (m)	35 (m)
				50 (w)
67 (w)	67 (m)	68 (br, m)	71 (m)	69 (w)
83 (w)	–	–		86 (w)
105 (w, sh)	115 (m, sh)	99 (w, sh)	99 (w)	104 (w, sh)
124 (s)	123 (s)	121 (s)	123 (s)	116 (s)

$Mn_2(CO)_{10}$	$Mn_2(CO)_9C(OC_2H_5)(CH_3)$	$Mn_2(CO)_9C(OC_2H_5)(C_6H_5)$	$Mn_2(CO)_9C(NHCH_3)(CH_3)$
55 (w)	–	57 (w)	–
62 (m)	–	–	–
72 (w)	83 (m)	89 (m)	–
94 (w)	103 (m)	105 (w)	103 (m)
117 (w)	125 (m)	134 (w)	–
164 (s)	153 (s)	156 (s)	158 (s)

[a] Frequencies reported as $\Delta\nu$ from the laser exciting frequency in cm^{-1}. [b] s = strong, m = medium, w = weak, br = broad, sh = shoulder.

contribution for dinuclear carbonyls [17], so that the mass effect upon ν(M–M) due to substitution in the *cis* position would be quite small. Both of these observations would suggest that the low $\Delta\nu$ Raman spectrum might distinguish between *cis* and *trans* substitution since the latter would be expected to result in somewhat larger shifts in ν(M–M) due to both bonding and mass effects.

The remainder of the low and middle frequency Raman spectra confirm the structural similarity within these two series of dinuclear metal carbonyl carbenes. The patterns of intensity and frequency are quite parallel within each series; for example, the rhenium compounds have bands in the ν(M–CO) and δ(M–C–O) regions occurring at about 395, 465, 480, 545, 600, and 615 cm^{-1} in each dirhenium carbene. These are very close in frequency to bands in the parent $Re_2(CO)_{10}$, while bands near 440, 495, and 635 for each carbene are not present in the parent compound.

Solid phase (Nujol) ir spectra in the middle frequency region provide evidence of the presence of the carbene ligand in the alkoxycarbenes. Peaks for the new $(CO)_9Re_2C(OC_2H_5)R$ are :C–O (1269, 1262 cm^{-1}), O–C_2H_5 (1137, 1140 cm^{-1}) and :C–R (974, 910 cm^{-1}) for R = CH_3 and C_6H_5 respectively, and are in agreement with assignments for similar manganese and rhenium complexes reported by Fisher [6, 7]. Assignment of the :C–N, N–CH_3, and :C–CH_3 vibrations in the aminocarbenes is not clear due to the presence of an intense broad peak in the 1150–1000 cm^{-1} region. This broad peak is very likely due to overlap of one or more vibrations such as :C–N, :C–N–C, and N–C [18], since there is apparently some double bond character to the :C–N bond. The :C–C vibration is observed at 970 cm^{-1} in the rhenium compound, but that region is obscured in the analogous manganese compound. The nmr chemical shifts (relative to internal TMS in d_6 acetone) for $(CO)_9Re_2C(OC_2H_5)CH_3$ are :C–CH_3, 2.99; O–CH_2, 4.65; CH_3, 1.53 and for $(CO)_9Re_2C(OC_2H_5)$-C_6H_5 are :C–C_6H_5, 7.45; O–CH_2, 4.31; CH_3, 1.50 with splitting patterns and relative intensities as expected. The considerable downfield shifts of the methylene and methyl groups directly attached to the carbene carbon are expected and are characteristic of an alkoxycarbene [6, 7, 19].

Isomerization of Syn$(CO)_9M_2C(NHCH_3)CH_3$ *(M = Mn, Re)*

Treatment of *syn*$(CO)_9Re_2C(NHCH_3)CH_3$ with KOH in anhydrous methanol failed to isomerize the carbene ligand to the *anti* configuration, as determined by nmr. Reaction with sodium tertiary butoxide, however, produced a *syn–anti* mixture. New peaks at 3330 and 1560 cm^{-1}, N–H stretching and bending respectively (Table II), indicated the presence of the new *anti* isomer. In the nmr spectrum a new doublet downfield (3.36 δ) from the *syn* N–CH_3 (3.09 δ) doublet and a new :C–CH_3 singlet downfield (2.90 δ)

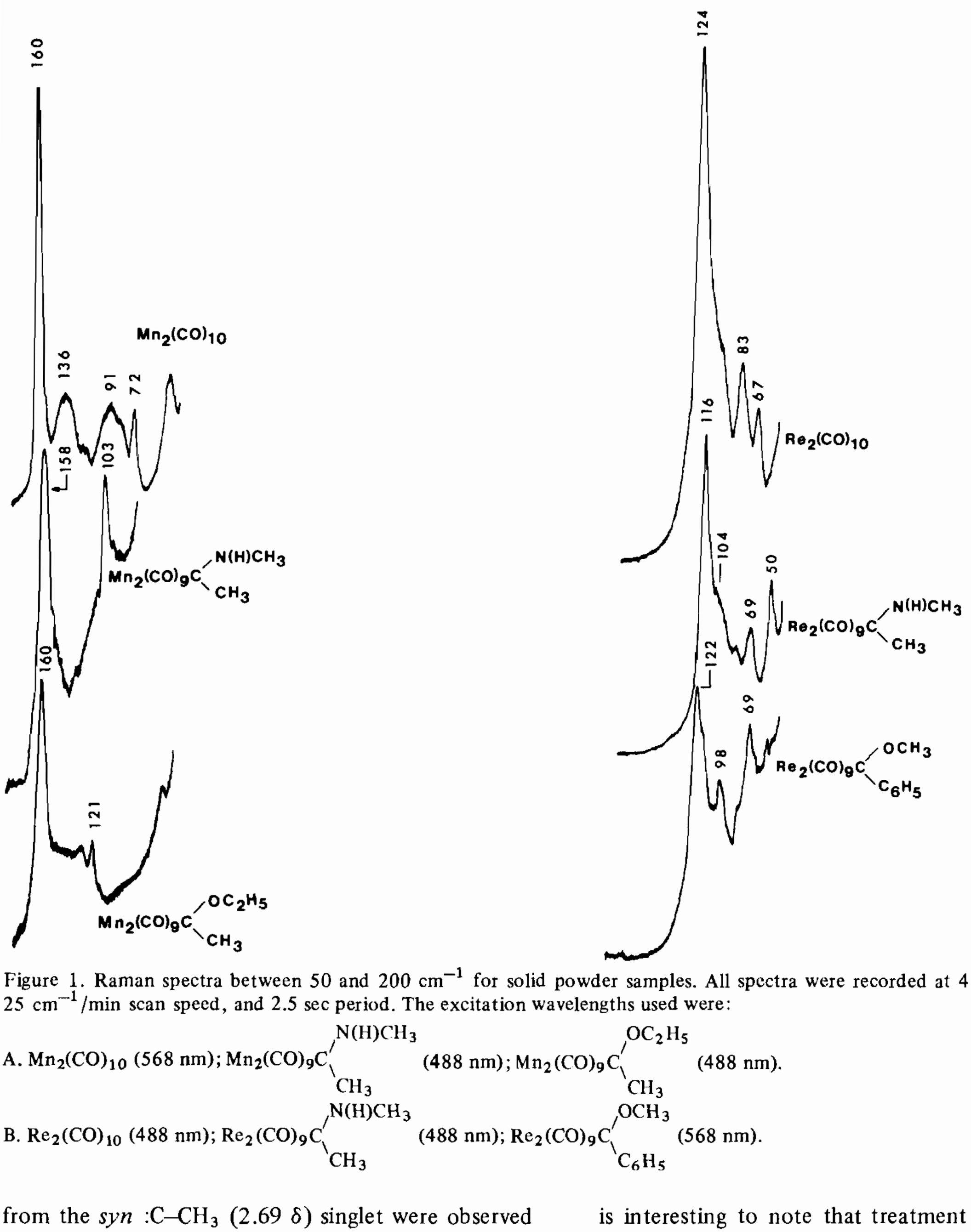

Figure 1. Raman spectra between 50 and 200 cm^{-1} for solid powder samples. All spectra were recorded at 4 cm^{-1} slit width, 25 cm^{-1}/min scan speed, and 2.5 sec period. The excitation wavelengths used were:

A. $Mn_2(CO)_{10}$ (568 nm); $Mn_2(CO)_9C\begin{smallmatrix}\diagup N(H)CH_3\\ \diagdown CH_3\end{smallmatrix}$ (488 nm); $Mn_2(CO)_9C\begin{smallmatrix}\diagup OC_2H_5\\ \diagdown CH_3\end{smallmatrix}$ (488 nm).

B. $Re_2(CO)_{10}$ (488 nm); $Re_2(CO)_9C\begin{smallmatrix}\diagup N(H)CH_3\\ \diagdown CH_3\end{smallmatrix}$ (488 nm); $Re_2(CO)_9C\begin{smallmatrix}\diagup OCH_3\\ \diagdown C_6H_5\end{smallmatrix}$ (568 nm).

from the *syn* :C–CH_3 (2.69 δ) singlet were observed (Table III) and assigned to the *anti* isomer on the basis of comparison to the data for the well documented *syn*- and *anti*$(CO)_5CrC(NHCH_3)CH_3$ [14]. Integration indicates that an approximate 6:4 *syn:anti* isomeric ratio was formed.

The results are significant for at least three reasons. First, the Re–Re bond is stable to these strongly basic conditions and the complex does not decompose. Second, the Nujol mull ir spectrum in the N–H stretching and bending regions gives preliminary information about the conformation of the methylaminomethylcarbenes whether bonded to a mono- or dinuclear metal carbonyl system. Third, it is interesting to note that treatment with sodium in tertiary butyl alcohol gave 90 and 100% *syn* to *anti* isomer conversion for $(CO)_5MC(NHCH_3)CH_3$ for M = Cr and W, respectively, but the presence of a *cis* triphenylphosphine ligand lowers the conversion to 0 and 75% for *cis*$(C_6H_5)_3P(CO)_4MC(NHCH_3)CH_3$, M = Cr and W respectively [14, 15, 20]. Under similar conditions we observed 0 and 40% *syn* to *anti* conversion for $(CO)_5M\text{-}M(CO)_4C(NHCH_3)CH_3$ where M–M is Mn–Mn and Re–Re respectively. These dinuclear carbenes are analogous to *cis*$(C_6H_5)_3P(CO)_4MC(NHCH_3)CH_3$ in that they have a $(CO)_5M$ ligand in the *cis* position relative to the aminocarbene ligand. Whether these results are due to kinetic or thermodynamic factors has not been determined, but visual observations of the color changes suggest the isomerization is fast relative to the total time given for the reaction, and thus the isomeric ratio obtained is probably a reflection of thermodynamic stabilities. The lowered amount of *syn* to *anti* isomerization when the $(C_6H_5)_3P$ or $(CO)_5M$ ligand is *cis* to the methylaminomethyl carbene could be due to their weaker π acceptor and stronger σ donor properties relative to CO [19, 21]. The presence of $(C_6H_5)_3P$ or $(CO)_5M$ in the *cis* position would be expected to cause more M–ligand π back-bonding in the M–carbene bond and make the carbene methyl or N–H protons less acidic and hence the carbene less susceptible to isomerization by the strong base, which in fact is what was observed. Similarly, the poorer π acceptor ability of the $(CO)_5M$ moiety relative to CO is the reason why the carbene ligand was formed in the *cis* position relative to the M–M bond in the first place since attack by LiR (R = CH_3 or C_6H_5) is thought to occur on the most electropositive carbon [22].

Treatment of *syn* $(CO)_9Mn_2C(NHCH_3)CH_3$ with methanolic potassium hydroxide or sodium tertiary butoxide gave no spectral evidence of an isomeric mixture, but considerable starting material was recovered in each attempt. At least some of the products were paramagnetic and very polar as exhibited by broadened nmr lines and strong binding to silica gel during chromatography. Although these products were not characterized, they very likely contained compounds resulting from Mn–Mn bond cleavage. The apparent degradation of the Mn–Mn system but not the Re–Re system under these conditions is consistent with the general relative stability of these carbenes to air oxidation whether as solids or in solution. Also the Mn–Mn carbenes are much more difficult to rid of paramagnetic impurities in the purification process, making the Re–Re carbenes clearly preferred for further study.

Conclusion

Low frequency Raman spectra of the series of compounds $(CO)_9M_2C(OR')R$ (M = Mn, Re; R = CH_3, C_6H_5; R' = CH_3, C_2H_5) and *syn* $(CO)_9M_2C(NHCH_3)CH_3$ (M = Mn, Re) show intense bands characteristic of ν(M–M) for dinuclear carbonyls of manganese and rhenium. The ν(M–M) bands are only slightly shifted to lower frequency compared to the corresponding bands of $M_2(CO)_{10}$ (M = Mn, Re). Substitution in a position *trans* to the M–M bond might be expected to cause more significant changes in ν(M–M) due to the greater mass effect which occurs when ligands along the extension of the M–M bond are changed or to the greater effect of the *trans* ligand bond on M–M bond strength. We predict, therefore, that the low $\Delta\nu$ Raman spectrum might be used to distinguish between *cis* and *trans* positions of substitution in dinuclear metal carbonyl carbenes.

The dinuclear methylmethoxycarbenes $(CO)_9M_2C(OCH_3)CH_3$ (M = Mn, Re) are easily converted, in good yield, to the corresponding methylaminomethylcarbenes. The reaction proceeds with retention of C_s symmetry, without apparent cleavage of the M–M bond, and the ligand is synthesized in the *syn* configuration. The *syn* isomer of $(CO)_9Re_2C(NHCH_3)CH_3$ is converted to a 6:4 *syn:anti* isomeric mixture by sodium tertiary butoxide (but not methanolic KOH) without apparent Re–Re cleavage. However, no evidence of *syn* to *anti* isomerization in $(CO)_9Mn_2C(NHCH_3)CH_3$ coud be obtained, perhaps due to Mn–Mn bond cleavage under the conditions used. The lower tendency of the dinuclear methylaminomethylcarbenes to undergo *syn* to *anti* isomerization compared to the Group VIB mononuclear compounds may be related to the presence of the $(CO)_5M$ moiety in the position *cis* to the carbene in the dinuclear Group VIIB compounds since the degree of *syn* to *anti* isomerization was also lowered by the presence of a *cis* $(C_6H_5)_3P$ ligand in the Group VIB compounds. Further studies on the *syn* to *anti* isomerization are needed on Group VIB carbenes having two $(C_6H_5)_3P$ ligands *cis* to the carbene and on Group VIIB carbenes having both $(CO)_5M$ and $(C_6H_5)_3P$ ligands cis to the carbene.

Acknowledgements

We thank Mr. Robert H. Block for assistance in the laboratory and the National Science Foundation, Grant GY-7663, the UW–Oshkosh Faculty Development Fund, and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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