

TRANSITION METAL CYANOCARBON DERIVATIVES

IV *. REACTIONS OF (1-CHLORO-2,2-DICYANOVINYL)PENTACARBONYLMANGANESE WITH TRIVALENT PHOSPHORUS AND RELATED LIGANDS

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Summary

Reactions of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ with trivalent phosphorus ligands or *t*-butyl isocyanide in boiling benzene do not result in the formation of dicyanovinylidene complexes but instead in the substitution of two CO groups to give the corresponding *fac*- $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ derivatives ($\text{L} = (\text{RO})_3\text{P}$ ($\text{R} = \text{CH}_3$ and C_2H_5) and $(\text{CH}_3)_3\text{CNC}$ or $\text{L}_2 = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{PR}'_2$ ($\text{R}' = \text{C}_6\text{H}_5$, $(\text{CH}_3)_2\text{N}$ and CH_3O)). The ditertiary phosphine $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ reacts with $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ even at room temperature with loss of the cyanocarbon residue to give *fac*- $[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]\text{Mn}(\text{CO})_3\text{Cl}$. Reaction of $\text{NaRe}(\text{CO})_5$ with $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$ gives the expected $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$ but only in mediocre yield (~11%).

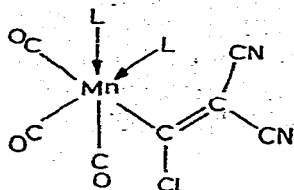
The thermal reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{M}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}$ and W) with trivalent phosphorus ligands have been shown [2,3] to result in the replacement of three carbonyl groups with two trivalent phosphorus ligands to give terminal dicyanovinylidene complexes of molybdenum and tungsten of the general type $\text{C}_5\text{H}_5\text{M}(\text{PR}_3)_2[\text{C}=\text{C}(\text{CN})_2]\text{Cl}$. In an attempt to prepare similar terminal dicyanovinylidene complexes of manganese we have now investigated analogous reactions of the manganese complex [4] $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ with related trivalent phosphorus ligands.

Reactions of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ with either the monodentate phosphorus ligands PR_3 ($\text{R} = \text{OCH}_3$ and OC_2H_5) or the bidentate phosphorus ligands $(\text{C}_6\text{H}_5)_2\text{-}$

* For part III see ref. 1. Portions of this work were presented at the 173rd National Meeting of the American Chemical Society, New Orleans, Louisiana, March, 1977: paper INOR 121 in abstracts.

$\text{PCH}_2\text{CH}_2\text{PR}_2$ ($\text{R} = \text{C}_6\text{H}_5$, OCH_3 , or $\text{N}(\text{CH}_3)_2$) in boiling benzene all led to the replacement of two carbonyl groups with two trivalent phosphorus atoms to give complexes with the general formula $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ (Table 1). A corresponding reaction of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ with triphenylphosphine failed to give a corresponding $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ derivative in significant quantities but instead led to extensive decomposition. Reaction of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ with excess $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ or $(\text{CH}_3\text{O})_3\text{P}$ in boiling toluene failed to give further carbonyl substitution beyond the *cis*- $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ stage but instead led to extensive decomposition. Heating $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ in boiling benzene either alone or in the presence of 1,3-cycloheptadiene, norbornadiene, or cycloheptatriene also led to extensive decomposition without the isolation of identifiable products.

The spectroscopic properties of the $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ derivatives (Table 2) are in accord with their formulations as the facial isomers I in which the trivalent phosphorus ligands are *trans* to CO groups. All of the $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ derivatives exhibit in their infrared spectra two strong $\nu(\text{CO})$ frequencies with the lower one always broadened. This is in accord with formulations as *fac*- $\text{L}_2\text{L}'\text{M}(\text{CO})_3$ derivatives [5,6] where the L and L' ligands are nearly equivalent electronically. Furthermore, the phosphorus-31 NMR spectrum of the complex $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]$ exhibits only a single resonance indicating that both phosphorus atoms of the symmetrical ditertiary phosphine are in identical environments. Since the ethane bridge of this ditertiary phosphine forces the phosphorus atoms to be in mutually *cis* positions in the manganese octahedron, the only possibility consistent with this single phosphorus-31 resonance is I ($2\text{L} = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$) with both phosphorus atoms *trans* to carbonyl groups. The trialkyl phosphite com-



(I)

plexes $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3[\text{P}(\text{OR})_3]_2$ also exhibit only a single phosphorus-31 resonance suggesting that both phosphite ligands are in equivalent environments.

The methyl ditertiary phosphine $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$, presumably because of the high basicity and low steric requirements of the two phosphorus atoms, reacts with $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ in benzene or tetrahydrofuran solution even at room temperature in contrast to the elevated temperatures required for the other ditertiary phosphines. The product, however, is not the expected *fac*- $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3\text{L}_2$ derivative since its infrared spectrum exhibits no $\nu(\text{CN})$ frequencies. On the basis of its infrared spectrum in the $\nu(\text{CO})$ region this product was identified as *fac*- $[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]\text{Mn}(\text{CO})_3\text{Cl}$. The reaction between $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ and $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ to give *fac*- $[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]\text{Mn}(\text{CO})_3\text{Cl}$ with chlorine transfer from carbon to manganese and complete loss of the cyanocarbon unit is completely analogous to the

(continued on p. 367)

TABLE 1
 PREPARATION AND PROPERTIES OF THE $fac-(NC)_2C=C(Cl)Mn(CO)_3L_2$ DERIVATIVES

Compound ^a	Preparation ^b		Color	M.p. (°C)	Analysis (Found (calcd.) (%))			
	Time (h)	Yield (%)			C	H	N	Cl
$fac-(NC)_2C=C(Cl)Mn(CO)_3[PF(OMe)_3]_2$	5	66	yellow	89-90	31.5 (31.3)	3.7 (3.6)	5.5 (5.6)	7.0 (7.1)
$fac-(NC)_2C=C(Cl)Mn(CO)_3[PF(OEt)_3]_2$	2	57	yellow	88	39.2 (39.1)	5.2 (5.1)	4.9 (4.8)	6.0 (6.1)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pf-Pf)$	4	95	white	175-178	61.1 (61.1)	3.7 (3.7)	4.3 (4.3)	5.4 (5.5)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pf-Pnm)$	16	44	light yellow	159-163	51.2 (51.5)	4.5 (4.5)	9.5 (9.6)	5.9 (6.1)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pf-Pom)$	6	24	yellow	155-160	49.4 (49.6)	3.6 (3.8)	5.0 (5.0)	6.3 (6.4)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(CNBu^t)_2$	4	65	tan	87	49.7 (48.9)	4.5 (4.6)	13.5 (13.4)	8.3 (8.5)

^a For an explanation of the ligand abbreviations see the Experimental. ^b Stoichiometric quantities of $(NC)_2C=C(Cl)Mn(CO)_5$ and the ligand L were heated in boiling benzene for the indicated period of time. The $fac-(NC)_2C=C(Cl)Mn(CO)_3L_2$ products were isolated in the indicated yields as described in the Experimental.

TABLE 2
SPECTROSCOPIC PROPERTIES OF THE $fac-(NC)_2C=C(Cl)Mn(CO)_3L_2$ DERIVATIVES

Compound ^a	Infrared spectrum (cm ⁻¹)		$\nu(C=O)$ ^c	Phosphorus-31 NMR spectrum (δ , ppm)	Proton NMR spectrum ^d (τ , ppm)
	$\nu(CN)$ ^b	$\nu(CO)$ ^b			
$fac-(NC)_2C=C(Cl)Mn(CO)_3(F(OMe)_3)_2$	2280m	2055s, 1970vs(br)	1443s	-161.2	CH ₃ : 6.17 (t, 6)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(F(OEt)_3)_2$	2234m	2054s, 1965vs(br)	1440s	-155.4	CH ₂ : 5.90 (m, 3, 6) CH ₃ : 8.62 (t, 7)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pi-Pi)$	2234m	2040s, 1957s(br)	1432s	-77.8	C ₆ H ₅ : 3.1 (br); CH ₂ CH ₂ : 7.9(br)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pi-Pnm)$	2226m	2039s, 1948s(br)	1421m	-165.6, -73.8	C ₆ H ₅ : ~2.5(d); CH ₃ : 7.20(d, 7) 7.36(d, 7)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(Pi-Pom)$	2234m	2042s, 1966vs(br)	1436s	-215.2, -77.7	C ₆ H ₅ : ~2.6(m); CH ₃ : 6.21(d, 8) 6.40(d, 10)
$fac-(NC)_2C=C(Cl)Mn(CO)_3(CNBu-t)_2$	2232m 2212s ^e 2192s ^e	2054s, 1976vs(br)	—	—	CH ₃ : 8.41 s

^a For an explanation of the ligand abbreviations see the experimental. ^b The infrared $\nu(CN)$ and $\nu(CO)$ frequencies were measured in CH_2Cl_2 solutions. ^c The infrared $\nu(C=O)$ frequencies were measured in KBr pellets. ^d s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; numbers in parentheses are coupling constants in Hz. ^e The 2212 and 2192 cm⁻¹ frequencies arise from the $\nu(CN)$ of the coordinated isocyanide ligands.

reported [3] reaction of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ with triphenylphosphine to give $\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$.

The reaction between $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and *t*-butyl isocyanide has been found [7] to result in isobutylene elimination to give two stereoisomers of the tricyanoethylene derivative $\text{C}_5\text{H}_5\text{Mo}[\text{CNC}(\text{CH}_3)_3]_2[(\text{NC})_2\text{C}=\text{CHCN}]\text{Cl}$. The reaction between $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ and *t*-butyl isocyanide under similar conditions proceeds with simple carbonyl substitution to give *fac*- $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]_2$ (I: L = $(\text{CH}_3)_3\text{CNC}$). The equivalence of the two *t*-butyl isocyanide ligands in this complex is suggested by the observation of a single methyl proton resonance.

In an attempt to extend this chemistry to rhenium, the required $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$, a new compound, was prepared from the reaction of $\text{NaRe}(\text{CO})_5$ with $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$. However, the yields of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$ are only ~11% based on $\text{Re}_2(\text{CO})_{10}$. This and the high cost of rhenium discouraged us from investigating reactions of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$ with Lewis base ligands. The much lower yields of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$ relative to its manganese analogue when prepared from $\text{NaMn}(\text{CO})_5$ and $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$ can be attributed to the much higher nucleophilicity [8] of $\text{NaRe}(\text{CO})_5$ relative to $\text{NaMn}(\text{CO})_5$. This can lead to unwanted side reactions including reaction of the second chlorine atom, which, in the case of the $\text{Re}(\text{CO})_5$ derivative, apparently results in decomposition rather than formation of a bridging dicyanovinylidene derivative [4] as in the case of the reaction between $\text{Cl}_2\text{C}=\text{C}(\text{CN})_2$ and $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$.

Experimental

Microanalyses (Table 1) were performed by Atlantic Microanalytical Laboratory, Atlanta, Georgia. Melting points (Table 1) were taken in capillaries and are uncorrected. Infrared spectra (Table 2) were taken in the indicated media (generally dichloromethane for $\nu(\text{CO})$ and $\nu(\text{CN})$ frequencies and KBr pellets for $\nu(\text{C}=\text{C})$ frequencies) and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics using the 1601 cm^{-1} band of polystyrene film for calibrating each spectrum. Proton NMR spectra (Table 2) were recorded on a Varian T-60 spectrometer at 60 MHz using CDCl_3 solutions. Phosphorus-31 NMR spectra (Table 2) were taken in CH_2Cl_2 solutions and recorded at 40.3 MHz on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. Phosphorus-31 NMR chemical shifts are reported in ppm above external 85% phosphoric acid.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling filtered solutions of organometallic compounds; (c) filling evacuated vessels containing organometallic compounds. Alumina (80 to 200 mesh) and silica gel for chromatography were used as received from Fisher Scientific. Tetrahydrofuran was redistilled over LiAlH_4 .

The manganese derivative $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_5$ was prepared by a combination of published procedures [4,9-11] using commercial $\text{CH}_3\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (Ethyl Corporation, New York, New York) and malononitrile (Kay-Fries Chemicals Inc., New York) as raw materials. The ligands $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ [12] (abbreviated as Pf-Pnm), $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$ [12] (abbreviated as Pf-Pom), and $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ [13] (abbreviated as Pm-Pm) were prepared

by the cited published procedures or minor variations thereof. The remaining trivalent phosphorus derivatives used in this work including $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) were commercial products and were used as received.

Reactions of $(NC)_2C=C(Cl)Mn(CO)_5$ with trivalent phosphorus ligands to give $fac-(NC)_2C=C(Cl)Mn(CO)_3L_2$ derivatives

Stoichiometric quantities of $(NC)_2C=C(Cl)Mn(CO)_5$ and the trivalent phosphorus ligand (4 to 12 mmol depending on the desired scale of the preparation) were boiled under reflux in 100 to 150 ml of benzene for the time indicated in Table 1. Solvent was then removed from the reaction mixture at 25°C/25 mmHg. The residue was chromatographed on an alumina column in dichloromethane solution. The yellow band of the product was eluted with dichloromethane. Evaporation of the eluate followed by crystallization from pentane in the cases of the trialkyl phosphite complexes or from mixtures of dichloromethane and hexane in the cases of the ditertiary phosphine complexes gave the $fac-(NC)_2C=C(Cl)Mn(CO)_3L_2$ derivatives in the yields indicated in Table 1.

The ditertiary phosphine complexes $fac-(NC)_2C=C(Cl)Mn(CO)_3(Pf-Pf)$ and $fac-(NC)_2C=C(Cl)Mn(CO)_3(Pf-Pom)$ formed crystalline 1/1 adducts with chloroform (identified by correct C, H, N and Cl analyses) when chloroform rather than dichloromethane was used in the above preparations.

Reaction of $(NC)_2C=C(Cl)Mn(CO)_5$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$

A mixture of 0.61 g (2 mmol) of $(NC)_2C=C(Cl)Mn(CO)_5$, 0.6 g (4 mmol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$, and 40 ml of tetrahydrofuran was stirred for 36 h. Solvent was removed from the deep green reaction mixture at 25°C/25 mmHg. A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The yellow band was eluted with dichloromethane. Evaporation of the dichloromethane eluate followed by crystallization of the yellow residue from a mixture of dichloromethane and pentane at -20°C gave 0.13 g (20% yield) of $fac-(Pm-Pm)Mn(CO)_3Cl$, m.p. 147–149°C, $\nu(CO)$ in CH_2Cl_2 : 2030s, 1948s, and 1900s cm^{-1} (lit. [14] $\nu(CO)$ for $fac-(Pm-Pm)Mn(CO)_3Cl$ in CH_2Cl_2 : 2021s, 1950s, and 1908s cm^{-1}).

Reaction of $(NC)_2C=C(Cl)Mn(CO)_5$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$ at room temperature in benzene rather than tetrahydrofuran solution also gave $fac-(Pm-Pm)Mn(CO)_3Cl$ but only in ~10% yield.

An authentic sample of $fac-(Pm-Pm)Mn(CO)_3Cl$ ($\nu(CO)$ in CH_2Cl_2 : 2030s, 1949s and 1901s cm^{-1}) was also prepared in 35% yield by reaction between 0.46 g (2 mmol) of $Mn(CO)_5Cl$ and 0.31 g (2 mmol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in 30 ml of tetrahydrofuran for 10 minutes at room temperature followed by crystallization of the resulting yellow solid from a mixture of dichloromethane and hexane at -20°C.

Reaction of $(NC)_2C=C(Cl)Mn(CO)_5$ with $(CH_3)_3CNC$

A mixture of 1.22 g (4 mmol) of $(NC)_2C=C(Cl)Mn(CO)_5$, 1.0 ml (0.7 g, 8.4 mmol) of t-butyl isocyanide, and 60 ml of benzene was boiled under reflux for 4 h. Solvent was removed at 25°C/25 mmHg. Recrystallization of the residue from a mixture of dichloromethane and hexane gave a total of 1.08 g of $fac-$

$(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mn}(\text{CO})_3[\text{CNC}(\text{CH}_3)_3]_2$ (65% yield), collected in two crops. The analytical samples were purified by a further crystallization from a mixture of dichloromethane and hexane.

Attempts to chromatograph this compound on alumina or Florisil columns in dichloromethane solution led to decomposition.

Preparation of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$

A solution of ~ 10 mmol of $\text{NaRe}(\text{CO})_5$ was prepared by stirring 3.26 g (5 mmol) of $\text{Re}_2(\text{CO})_{10}$ in 90 ml of tetrahydrofuran for 8 h at room temperature with 12 mmol of sodium as 1% sodium amalgam. After removal of the excess mercury the $\text{NaRe}(\text{CO})_5$ solution was cooled to -78°C and then treated dropwise with a solution of 1.46 g (10 mmol) of 1,1-dichloro-2,2-dicyanoethylene in 20 ml of tetrahydrofuran. The red-brown reaction mixture was stirred at -78°C for 2 h, and then at room temperature for 4 h. Solvent was then removed from the reaction mixture at $25^\circ\text{C}/30$ mmHg. The residue was extracted with 400 ml of dichloromethane in three portions. These extracts were filtered through Celite. The filtrate was evaporated at $25^\circ\text{C}/25$ mmHg. The residue was chromatographed on a silica gel column prepared in hexane. The yellow band was eluted with 1/1 dichloromethane/hexane. Concentration of the eluate to ~ 15 ml gave 0.47 g (11% yield) of yellow crystalline $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Re}(\text{CO})_5$, m.p. $136\text{--}137^\circ\text{C}$ (dec.); infrared spectrum: $\nu(\text{CN})$ in CH_2Cl_2 : 2235w cm^{-1} ; $\nu(\text{CO})$ in CH_2Cl_2 : 2165m and 2055s cm^{-1} ; $\nu(\text{C}=\text{C})$ in KBr: 1480w cm^{-1} . Anal. Found: C, 24.5; H, 0.0; N, 6.4; Cl, 8.1. $\text{C}_9\text{ClN}_2\text{O}_5\text{Re}$ calcd.: C, 24.7; H, 0.0; N, 6.4; Cl, 8.1%.

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References

- 1 R.B. King and M.S. Saran, *Inorg. Chem.*, **14** (1975) 1018.
- 2 R.B. King and M.S. Saran, *Chem. Commun.*, (1972) 1053.
- 3 R.B. King and M.S. Saran, *J. Amer. Chem. Soc.*, **95** (1973) 1817.
- 4 R.B. King and M.S. Saran, *J. Amer. Chem. Soc.*, **95** (1973) 1811.
- 5 F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, **84** (1962) 4432; F.A. Cotton, *Inorg. Chem.*, **3** (1964) 702.
- 6 L.W. Houk and G.R. Dobson, *J. Chem. Soc. A*, (1966) 317; *Inorg. Chim. Acta* **1** (1967) 287; *Inorg. Chem.*, **5** (1966) 2119.
- 7 M.S. Saran and R.B. King, paper presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pennsylvania, April, 1975; paper INOR 25 in abstracts; R.B. King, M.S. Saran, D.P. McDonald, and S.P. Diefenbach, manuscript in preparation.
- 8 R.E. Dessy, R.L. Pohl and R.B. King, *J. Amer. Chem. Soc.*, **88** (1966) 5121.
- 9 R.B. King, J.C. Stokes and T.F. Korenowski, *J. Organometal. Chem.*, **11** (1968) 641.
- 10 K. Friedrich, *Angew. Chem. Int. Ed.*, **6** (1967) 959.
- 11 A.D. Josey, C.L. Dickinson, K.C. Dewhirst and B.C. McKusick, *J. Org. Chem.*, **32** (1967) 1941.
- 12 R.B. King and W.F. Masler, *J. Amer. Chem. Soc.*, **99** (1977) 4001.
- 13 S.A. Butter and J. Chatt, *Inorg. Syn.*, **15** (1974) 185.
- 14 J.A. Connor and G.A. Hudson, *J. Organometal. Chem.*, **73** (1974) 351.