

APPLICATION OF HIGH PRESSURE SPECTROSCOPY TO THE STUDY OF INTERACTIONS OF SMALL GASEOUS MOLECULES WITH TRANSITION METAL COMPLEXES AND ORGANOMETALLIC COMPOUNDS

II *. INTERACTION OF VANADIUM(II) AND MOLYBDENUM(II) PHOSPHINE COMPLEXES WITH CO

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Summary

The usefulness of high pressure infrared spectroscopic studies as a preliminary step in inorganic syntheses is illustrated. The reactivity of the transition metal complexes $[\text{VCl}_2(\text{PEt}_3)_2]_2$ and $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ with CO, N_2 , and H_2 was screened. The reversible reaction of $[\text{VCl}_2(\text{PEt}_3)_2]_2$, and the irreversible reaction of $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ with CO under pressure are described.

Introduction

In our first paper we reviewed the published applications of high pressure spectroscopy (40–450 atm) to inorganic and organometallic systems, and provided an example of the use of high pressure infrared spectroscopy in detecting the existence of a thermodynamically unstable complex [1]. Because the uses and limitations of this relatively unfamiliar technique to inorganic chemistry need amplification, we are reporting our utilization of high pressure infrared spectroscopy to screen transition metal complexes for their reactivity towards small gaseous molecules, to demonstrate the reversibility of adduct formation, to measure the relative rates of intermediate and product formation, and to establish the attainment of the state of thermodynamic equilibrium for a reaction system. The use of high pressure infrared spectroscopy specifically for screening reactivity was first reported by King and his coworkers [2].

Information obtained by high pressure techniques is useful in designing synthetic experiments. High pressure infrared spectroscopy was used in an imaginative way to determine the reaction time and best temperature and pressure conditions for synthesizing the then unknown compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{-}$

* For part I see ref. 1.

$W(CO)_3]_2$ from $[(\eta^5-C_5Me_5)W(CO)_2]_2$ [3]. Reaction conditions necessary for synthesizing thermodynamically unstable, but moderately inert *trans*- $Mo(CO)_2$ -(dppe) $_2$ from *trans*- $Mo(N_2)_2(dppe)_2$ were established by high pressure infrared spectroscopy [4].

A V^{II} -system was chosen for screening because there is evidence that it is the +2 oxidation state which is the active form that binds and fixes dinitrogen [5–9]. The compound $Mo_2Cl_4(PEt_3)_4$ was chosen because it represented a class of compounds in which there is a strong metal–metal quadruple bond, and for which there was no information at the time we started our experiments on the reactivity of these compounds with small gaseous molecules. Several reports on the reactions of transition metal complexes containing metal–metal triple bonds with small gaseous molecules have appeared, however. For example, the alkoxy compounds $Mo_2(OR)_6$ react reversibly with CO to give diamagnetic $Mo_2(OR)_6(CO)$ [10], CO_2 reacts with $Mo_2Et_2(NMe_2)_4$ in a reductive elimination reaction to produce $Mo_2(O_2CNMe_2)_4$ [11], $Re_2Cl_4(PR_3)_4$ ($R = Et$ or Pr^n) reacts with CO at one atmosphere to form the $17 e^-$ -complex, *trans*- $ReCl_2(CO)_2$ -(PR_3) $_2$ [12], $[(Me_5C_5)Mo(CO)_2]_2$ gives $[(Me_5C_5)Mo(CO)_2NO]$ when reacted with NO [13], and $[(Me_5C_5)M(CO)_2]_2$ ($M = Cr, Mo, W$) are formed by the action of CO on $[(Me_5C_5)M(CO)]_2$ [3].

The compounds $[VCl_2(PEt_3)_2]_2$ and $Mo_2Cl_4(PEt_3)_4$ were screened by high pressure infrared spectroscopy for their reactivity to H_2 , N_2 and CO. The spectrum of $[VCl_2(PEt_3)_2]_2$ remains unaltered when a benzene solution is exposed to 2150 psig (146 atm) of dinitrogen for 24 h at ambient temperatures, or when the solution is subjected to 146 atm of dihydrogen for 138 h. Similarly, there is no change in the spectrum of $Mo_2Cl_4(PEt_3)_4$ in toluene when the solution is subjected to dinitrogen pressures of 139 atm for 64 h, nor when the solution is under 136 atm of dihydrogen for 25.5 h. Both systems were studied at ambient temperature.

On the other hand, the interaction of these two compounds with carbon monoxide is sufficiently strong as to be detectable by high pressure infrared spectroscopy. The purpose of this report is to demonstrate how high pressure infrared spectroscopy can be used to collect information important to the design of experiments for synthesizing new compounds.

Results and discussion

All evidence indicates that the predominant, if not the only vanadium species in a benzene solution of dichlorobis(triethylphosphine)vanadium(II) is the dimer. The molecular weight was shown by cryoscopy to be 709 ± 65 , which compares favorably with 716 for the dimer. The electronic spectrum contains three $d-d$ transition bands at 10.04 kK (ϵ 21), 15.12 kK (ϵ 19), and 22.5 kK (ϵ 30). The positions and relative intensities of the bands in this spectrum compare closely to those of other VCl_2L_2 complexes, which are also oligomeric [14].

A low value of 1.98 B.M. for the effective magnetic moment of the crystal-line $[VCl_2(PEt_3)_2]_2$ remains unchanged when the solid is dissolved in benzene. This value of the magnetic moment is considerably lower than the spin-only value for a d^3 -system, 3.87 B.M. This behavior is consistent with a dimeric

TABLE 1

TIME-DEPENDENT CHANGES IN RELATIVE INTENSITIES OF INFRARED-ACTIVE BANDS IN SELECTED REGIONS OF THE SPECTRUM OF A $3.97 \times 10^{-1} M$ BENZENE SOLUTION OF $[\text{VCl}_2(\text{PEt}_3)_2]_2$ EXPOSED TO CO OR He AT 1400 PSIG (95 ATM)

Spectrum No. (gas)	Time of Exposure to Gas (h)	Bands (cm^{-1})				
		2070	2040	1880	1855	410
1(He)	0	—	—	—	—	vw
2(CO)	0.25	—	w-m	sh	vw	vw
3(CO)	1.1	w-m	m	s	s	m
4(CO)	1.7	w-m	m	s	vs	m-s
5(He)	1.1	—	w	m	m-s	m
6(He)	2.0	—	vw	w	m-s	w-m
7(He)	42.0	—	—	—	vw	vw
8(CO)	5.5	m	w-m	s	vs	m-s
9(He)	52.5	—	—	—	s	vw
10(He)	170.0	—	—	—	s	vw
11(CO)	0.25	—	w-m	—	s	vw

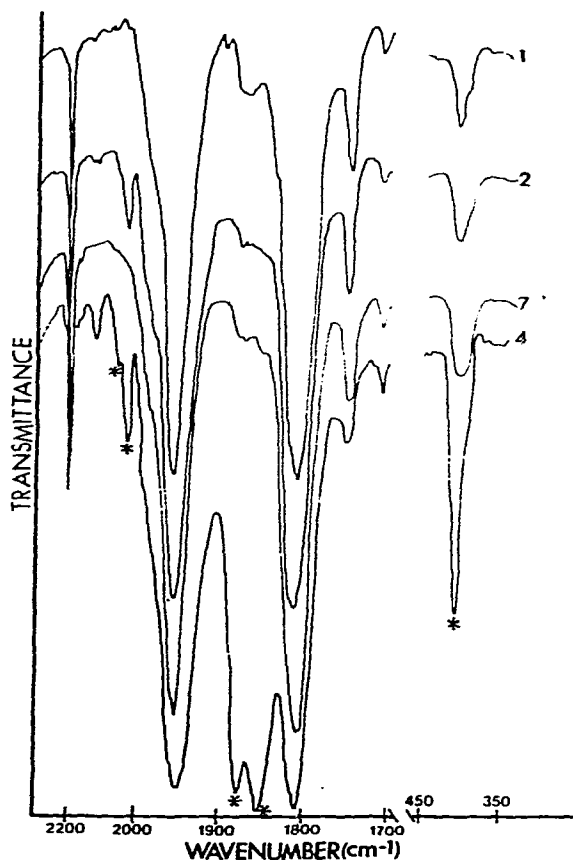


Fig. 1. Time-dependent effect of CO pressure (1400 psig) on bands in selected regions of the infrared spectrum of a $3.97 \times 10^{-1} M$ $[\text{VCl}_2(\text{TEP})_2]_2$ in benzene solution. Spectra numbers refer to the following conditions: 1. Solution under He gas (1400 psig) at time zero; 2. Solution under CO for 0.25 h; 4. Solution under CO for 1.7 h; 7. Solution after replacement of CO for 1.7 h by He for 42 h.

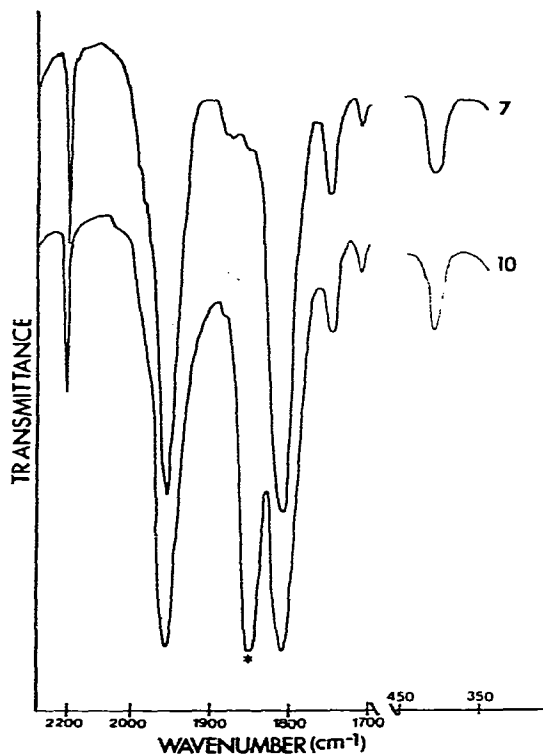


Fig. 2. Time-dependent effect of CO pressure (1400 psig) on bands in selected regions of the infrared spectrum of a $3.97 \times 10^{-1} M$ benzene solution of $[\text{VCl}_2(\text{PEt}_3)_2]_2$. Spectra numbers refer to the following conditions: 7. Solution after successive exposure to He for 42 h and CO for 1.7 h; 10. Solution after exposure to He for 170 h and CO for 5.5 h.

structure and suggests metal-metal interaction. Other crystalline VCl_2L_2 compounds also have lower than expected values for their effective magnetic moments. The magnitudes of these moments are highly temperature dependent and are attributed to antiferromagnetic interaction in a polymeric structure [15].

When benzene solutions of $[\text{VCl}_2(\text{PEt}_3)_2]_2$ are subjected to carbon monoxide pressures of 1400 psig (95 atm) at ambient temperatures, several changes occur in the infrared spectrum of the solution. These changes are summarized in Table 1.

Within 15 minutes after exposure to CO pressure, a distinct carbonyl stretching vibration appears at 2040 cm^{-1} . The band at 2040 cm^{-1} appears, as shown in spectrum 2 of Fig. 1, before any other carbonyl band. (The band at 2140 cm^{-1} is due to the CO stretching vibration of dissolved, uncomplexed carbon monoxide.) When a solution that is first subjected to CO pressure is relieved of this pressure and placed under helium at 95 atm, the 2040 cm^{-1} band rapidly disappears. Spectrum 7 of Fig. 1 and spectrum 10 of Fig. 2 show that the species responsible for this band is formed reversibly over two cycles. The complex responsible for this band is formed and dissociates at a rate much greater than any other product which results from this reaction. Almost cer-

tainly this reaction intermediate is formed by a simple Lewis acid–base interaction between $[\text{VCl}_2(\text{PET}_3)_2]_2$ and carbon monoxide.

With the passage of time, additional carbonyl bands begin to appear in the infrared spectra at 2070, 1880, and 1855 cm^{-1} , and the band at 410 cm^{-1} intensifies. The peaks at 2070, 1880, and 410 cm^{-1} shown in spectrum 4 of Fig. 1 increase in intensity at a rate slower than the rate of appearance of the 2040 cm^{-1} band, but more rapidly than the 1855 cm^{-1} band. The band at 410 cm^{-1} is not assigned, but it is due either to a V–C or V–Cl stretching vibration of a carbonyl chloride intermediate. It diminishes in intensity when the system is placed under a high pressure of helium after the CO pressure is reduced. The species responsible for the 2070, 1880, and 410 cm^{-1} band intensification are formed reversibly over two cycles as shown in spectrum 7 of Fig. 1 and spectrum 10 of Fig. 2.

The product responsible for the carbonyl band at 1855 cm^{-1} is formed and dissociates at a rate much slower than any of the other carbonyls. For reaction times less than 1.7 h, the 1855 cm^{-1} band appears reversibly as shown in spectrum 7 of Fig. 1. However, the concentration of the product giving rise to the band at 1855 cm^{-1} when the $[\text{VCl}_2(\text{PET}_3)_2]_2$ solution has been under CO pressure for 5.5 h, is so great as not to be fully decomposed even after the solution

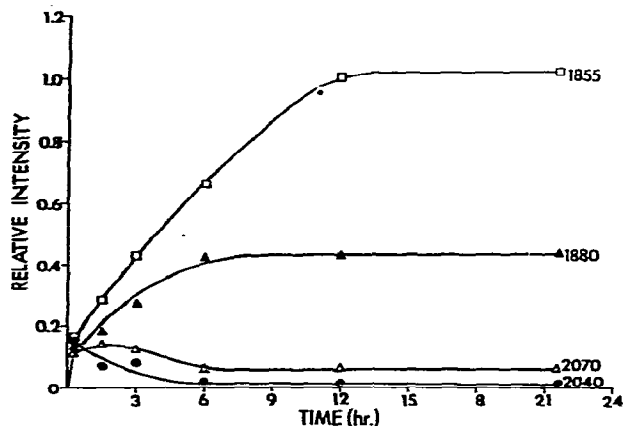


Fig. 3. Relative intensities of carbonyl stretching vibrations of products arising from the reaction of $[\text{VCl}_2(\text{PET}_3)_2]_2$ (0.20 M) and CO (88 atm) in benzene at room temperature. All intensities are normalized to the 1810 cm^{-1} band of the solvent benzene.

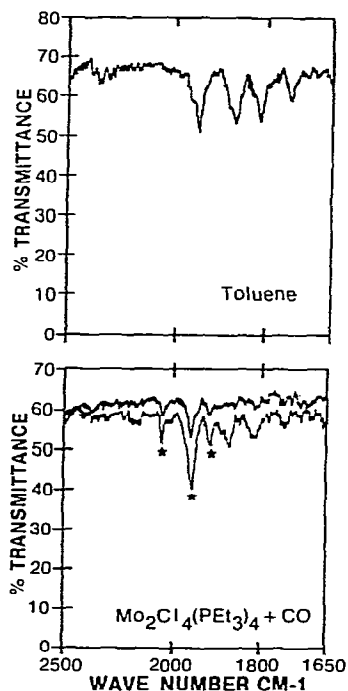


Fig. 4. Infrared spectrum of a saturated solution of $\text{Mo}_2\text{Cl}_4(\text{PET}_3)_4$ in toluene after reaction with CO. Bands marked with * are due to carbonyl stretching vibrations. The first spectrum is that of toluene under helium at 52 atm.

has been under 95 atm helium for 170 h (Fig. 2).

In a separate experiment a 0.20 M benzene solution of $[\text{VCl}_2(\text{PEt}_3)_2]_2$ was subjected to 1300 psig (88 atm) of CO at room temperature. The intensities of the carbonyl bands, normalized to the intensity of the 1810 cm^{-1} band of the solvent benzene, were measured as a function of time. These are shown in Fig. 3. The system is seen to achieve a state of thermodynamic equilibrium in a period of approximately 12 h. A spectrum taken after 50.0 h showed that the concentrations of the product species were unaltered from those at 21.5 h. The actual concentrations of the product species cannot be obtained by this method, but the existence of a state of thermodynamic equilibrium can be established.

The results of this high pressure infrared study leave no doubt that $[\text{VCl}_2(\text{PEt}_3)_2]_2$ reacts slowly with CO under pressure to give at least three carbonyl species. The thermodynamic stability of the species which gives rise to the 1855 cm^{-1} band is sufficient to allow isolation. This compound is most likely a $15 e^-$ *trans*-(CO) $_2\text{VCl}_2(\text{PEt}_3)_2$ complex analogous to the $17 e^-$ rhenium complex reported earlier [12]. The $17 e^-$ V^{II} carbonyl, $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCO}$, gives a spectrum with a carbonyl vibration at 1881 cm^{-1} [16]. To the best of our knowledge the only other V^{II} carbonyl complexes which have sufficient thermodynamic stability for characterization are $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_3(\text{PPh}_3)][\text{PF}_6]$ and $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2(\text{dppe})\text{X}$ ($\text{X} = \text{BF}_4^-, \text{PF}_6^-$) [17].

Previously, it had been reported that $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$, which contains a Mo—Mo quadruple bond, does not react to form a carbonyl when a refluxing ethanol, acetonitrile, or toluene solution is subjected to one atmosphere of carbon monoxide [12]. Under the same conditions the Re—Re triple bond in $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ is broken to give *trans*- $\text{Re}(\text{CO})_2\text{Cl}_2(\text{PEt}_3)_2$. We have observed that when a saturated solution of $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ in toluene is subjected to 760 psig (52 atm) of CO at room temperature there is a slow chemical reaction which gives rise to three carbonyl bands at 2032, 1947, and 1904 cm^{-1} (Fig. 4). (There is no absorption in the carbonyl region of saturated solutions of $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ in toluene other than four weak bands due to the solvent.) The reaction is irreversible. To our knowledge this is only the second example of a reaction between a small gaseous molecule with a transition metal complex having a metal—metal quadruple bond. Complexes of the type $\text{Mo}_2\text{X}_4\text{L}_2$ (where $\text{X} = \text{Cl}$ or Br and $\text{L} = \text{PEt}_2\text{Ph}$, PEt_3 or PBu_3^{n}) react with NO at 1 atm to give low yields of $\text{Mo}(\text{NO})_2\text{X}_2(\text{PR}_3)_2$ [17].

High pressure spectral studies of $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ in toluene were hampered by the low solubility of the phosphine complex. Despite the low intensity of the bands, the spectrum was highly informative in that it revealed the existence of one or more thermodynamically stable or inert carbonyls which can be isolated in future preparative experiments.

Experimental

Purification of reagents and solvents

Benzene, hexane, and toluene (MCB spectroquality or reagent grade) were purified by fractional distillation from alkali metals under argon. The solvents were partially degassed and stirred over sodium metal before being transferred

into storage reservoirs, which were degassing apparatus of Taylor's design [19] as modified by Creek [20].

Tetrahydrofuran (Fischer, certified) was dried by refluxing with potassium naphthalenide, and then it was distilled under argon into a storage reservoir.

Triethylphosphine (Pfaltz and Bauer or Aldrich) was predistilled under argon onto sodium wire. The distillate was refluxed with sodium for 10 h and then fractionally distilled under argon onto fresh sodium wire. The constant boiling fraction, 127–127.5°C, was retained. The pure triethylphosphine was degassed by the alternating freeze-thaw method and stirred over sodium before being transferred into a storage vessel.

The compressed gases, carbon monoxide (Matheson, CP), hydrogen (Airco, grade 5), and helium (Linde) were used as supplied by the manufacturers. Nitrogen (Airco, grade 5) was passed through a Model 98 HP purifier, supplied by Airco, to remove trace oxygen and water.

Preparation of starting materials

$Mo_2Cl_4(PEt_3)_4$. Tetrachlorotetrakis(triethylphosphine)dimolybdenum(II) was synthesized in accordance with previously-published instructions [20].

$VCl_2(THF)_2$. A 57.1 mmol quantity of anhydrous vanadium trichloride (K and K or Alfa Inorganics) or tris(tetrahydrofuran)vanadium(III) chloride was weighed under argon into a baked paper thimble and placed in a Soxhlet extractor. The solid was extracted for three to four days with 120 ml THF onto 2.07 g (31.7 mmol) zinc. The dark green solution was filtered, and the pale green precipitate was washed twice with 25 ml portions of THF. The solid was dried overnight under vacuum, transferred in the drybox to another thimble, and extracted for three days with approximately 200 ml of THF. The extract was filtered, and the precipitate was dried under vacuum overnight. The yield of pale green $VCl_2(THF)_2$ was 14.59 g (96%) based on the quantity of the vanadium(III) starting material.

Anal. Found: Cl, 27.40; Cl, 27.00; C, 34.92; H, 5.82; V, 18.71. Calcd. For $C_8H_{16}Cl_2O_2V$: Cl, 26.65; C, 36.11; H, 6.07; V, 19.14%.

$[VCl_2(PEt_3)_2]_2$. Bis(triethylphosphine)vanadium(II) chloride may be prepared by the zinc reduction of $VCl_3(PEt_3)_2$. However, since $VCl_2(THF)_2$ is easily prepared, purified, and handled, we preferred using the THF complex as the starting material.

A 12.45 g (46.8 mmol) sample of $VCl_2(THF)_2$ was placed in a Schlenk tube in a dry box, and 50 ml of freshly distilled benzene was added with vigorous stirring. Upon the addition of 14.4 ml (97.3 mmol) triethylphosphine, the light green solid dissolves immediately, to give a dark green solution. The total volume of the solution was reduced to about 35 ml, and the solution was then filtered. Approximately 200 ml of freshly distilled and degassed hexane was added dropwise to the vigorously stirred filtrate. The resulting dark green precipitate was removed by filtration and washed with hexane until the filtrate was clear. The yield was 12.32 g (73.5%) of an extremely oxygen-sensitive material.

Anal. Found: Cl, 19.52, 20.01. Calcd. for $C_{12}H_{30}Cl_2P_2V$: Cl, 19.81%. Chloride analyses were performed in our laboratory by a standard potentiometric method. Because of the extreme oxygen-sensitivity of the compound, commercial analysis were found to be unreliable.

Physical methods

Elemental analyses were by Galbraith Laboratories Inc., Knoxville, Tennessee.

Solvents and other volatile liquids were transferred by standard techniques on an all glass vacuum line or under argon by Schlenk techniques.

Magnetic susceptibility measurements. Magnetic susceptibilities of crystalline compounds were measured by the Faraday method. Mercury(II) tetrathio-cyanatocobalt(II) was used as the calibrant. All samples were loaded in a dry-box and blanketed with argon during the measurement of the susceptibilities. All measurements were made at 296 K. Molar magnetic susceptibilities were corrected for diamagnetic contributions of the ligands and metal ions by application of Pascal's constants.

Magnetic susceptibilities of samples in benzene solution were measured by the Evans method [22]. Concentrations were corrected for temperature effects [23]. The value of $\mu_{\text{eff}}^{30\text{K}}$ for $[\text{VCl}_2(\text{PEt}_3)_2]_2$ in benzene is 1.98 B.M. ($\chi_g = 3.78 \times 10^{-6}$ cgsu). NMR spectra were taken on a 90 MHz Perkin-Elmer Model 32 spectrometer.

High pressure infrared measurements. The high pressure reactor and cell used in these experiments have been described previously [1]. The pressure cell was equipped with KRS-5 (Harshaw) windows.

Infrared measurements were made either on a Beckman IR-10 or a Perkin-Elmer Model 225 spectrophotometer.

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