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GROUP VI METAL PENTACARBONYL COMPLEXES OF 1,2,4-TRIAZOLES

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Summary

The synthesis of chromium and tungsten pentacarbonyl complexes with 4-methyl and 4-phenyl-1,2,4-triazole is reported. The nature of the lowest energy absorption in the ultraviolet spectra of these complexes has been examined and shown to be principally a ligand field band. The triazoles are shown to be acting as monodentate ligands by infrared and ^{1}H nuclear magnetic resonance spectroscopy. The compounds show strong solvent dependence in the ^{1}H NMR and these effects are explained by solvent—solute interaction. The temperature dependence of the ^{1}H NMR spectrum of $W(CO)_5$(4-phenyl-1,2,4-triazole) has also been examined.

Introduction

Group VI $M(CO)_5L$ complexes in which L is a nitrogen donor ligand have been the subject of wide interest [1], and compounds with pyridine and its derivatives have been studied extensively [2]. Metal pentacarbonyl complexes with pyrazole, imidazole, thiazole and isothiazole have been studied [3] and also a number of papers concerning transition metal complexes of 1,2,4-triazoles have been published [4]. No metal carbonyl complexes with triazoles have been reported to our knowledge. 4-Substituted 1,2,4-triazoles are known for their ability to act both as monodentate and bidentate ligands [4b]. In most cases they act as bidentate ligands bridging two metal atoms. This can result in the formation of dimeric, trimeric or polymeric species, but only a few monomeric species have been reported [5].

In this paper we report the first examples of metal carbonyl complexes with 1,2,4-triazole derivatives (see Fig. 1). Complexes of $Cr(CO)_5$ and $W(CO)_5$ with

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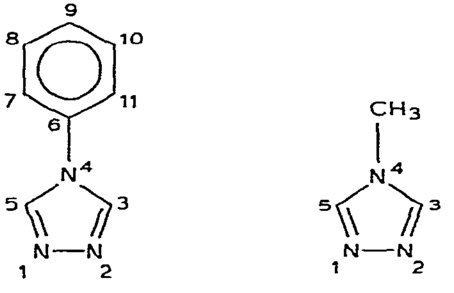
4-phenyl-1,2,4-triazole (Phtrz) and 4-methyl-1,2,4-triazole (Metrz) were prepared and their spectroscopic data are discussed with respect to the nature of the coordination of the ligands. The temperature and solvent dependence of the ^1H NMR spectra of $W(CO)_5Phtrz$ have been studied and this suggests a strong interaction between the triazole ligand and the solvent.



(1) (2)

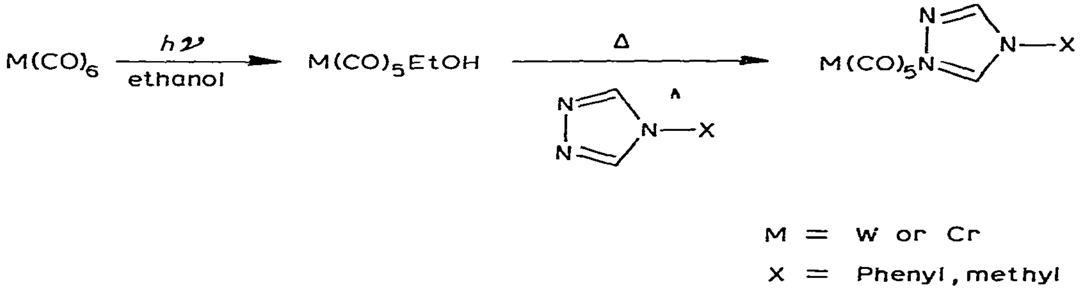
Fig. 1. Ligands: (1) 4-phenyl-1,2,4-triazole, (2) 4-methyl-1,2,4-triazole.

Results and discussion

Preparation

$W(CO)_5$ and $Cr(CO)_5$ complexes of Phtrz and Mertz were prepared by initial photolysis of a suspension of the metal hexacarbonyl in ethanol. After the photolysis, the ligand was added to the solution of the metal pentacarbonyl solvent adduct (see Scheme 1). The solvent was then removed under reduced pressure at room temperature. The crude product was purified by passage down a small column of neutral alumina using acetone as eluant. The complexes were further purified by recrystallisation from ethanol. Yields greater than 70% were obtained and elemental analysis in all cases was found to be consistent with the proposed product. All the compounds were found to be air stable both in the solid state and in solution. We have no evidence for the formation of dimeric species.

SCHEME 1



Electronic spectroscopy

The nature of the lowest energy absorption in $M(CO)_5L$ complexes (M = W, Cr, L = N-donor) has been subject of intensive investigation [1,2]. It is generally agreed that the band observed at approximately 400 nm has substantial ligand field character, although N-donor ligands with low lying π^*-orbitals also exhibit metal—ligand charge transfer (MLCT) bands in this region.

The compounds reported in this work all have a lowest energy absorption maximum near 400 nm (see Table 1). This band shows only slight solvent dependence (see Fig. 2), and this suggests that it contains little contribution from a MLCT transition. This is not surprising, since it is expected that the energy of the π^*-orbitals is quite high [3] and therefore the MLCT band would occur under the intense carbonyl π—π^* transitions at about 260 nm. Apart from these carbonyl transitions no other absorptions were observed in the ultraviolet region. The tungsten compounds also exhibit a weak shoulder at the low energy side of the 400 nm absorption and this can be assigned to the singlet—triplet transition $^1A_1 \rightarrow {}^3E$.

The nature of the photoactive state in $M(CO)_5L$ complexes continues to be subject of controversy [2,6,7]. In solution at room temperature, visible irradiation leads to loss of the unique ligand. The efficiency of this process appears to be dependent on the nature of the lowest energy excited state. It has been suggested that a ligand field excited state leads to loss of the unique ligand with a greater efficiency than a MLCT state [1]. In order to determine the probable nature of the lowest excited state, we measured the quantum efficiency for the loss of unique ligand (Φ_{diss}) in reaction I at 436 nm irradiation. A Φ_{diss} value of 0.6 ± 0.1 was obtained and this high efficiency is indicative of a lowest energy ligand field excited state.

$$W(CO)_5Phtrz \xrightarrow[\text{benzene/pentene} \atop (50/50\ v/v)]{h\nu} W(CO)_5\text{pentene} + Phtrz \qquad (1)$$

Infrared spectroscopy

Vibrational spectroscopy has been used extensively for the characterisation of both carbonyl [8] and triazole complexes [4]. The CO centred vibrations, which are consistent with a $M(CO)_5$ species, have been listed in Table 2. ν(CO)

TABLE 1

ELECTRONIC SPECTRA OF THE $M(CO)_5L$ COMPLEXES

Compound	λ_{max} in nm (ϵ)		Solvent
	$^1A_1 \rightarrow {}^1E$	$^1A_1 \rightarrow {}^3E$	
$W(CO)_5Phtrz$	395(3500)	425(1300)	toluene
	389	425(sh)	ethanol
$W(CO)_5Metrz$	390(2800)	425(900)	ethanol
$Cr(CO)_5Phtrz$	402		toluene
	397(2200)		ethanol
$Cr(CO)_5Metrz$	398(2700)		ethanol

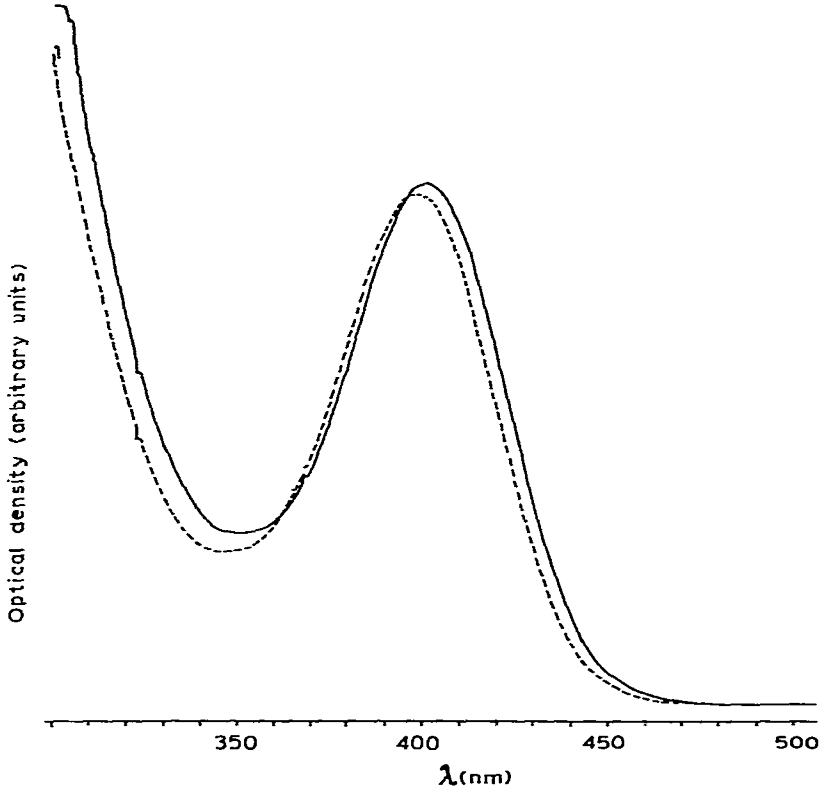


Fig. 2. The ultraviolet/visible spectrum of $Cr(CO)_5$Metrz in ethanol (— — — —) and toluene (————).

frequencies were obtained in toluene, in KBr only broad bands are observed which are often split because of lattice effects. The ν(MC) and β(MCO) vibrations show the expected metal dependence [3,7,8].

TABLE 2

CARBONYL VIBRATIONS OF $M(CO)_5$ TRIAZOLE COMPLEXES (cm^{-1})

Compounds	ν(CO) [a]	β(MCO) [b]		ν(MC) [b]			
$W(CO)_5$Phtrz	2075w 1927vs 1900vs	592(sh) 581vs	548m	480w	440w 430w 420w	405w	382(sh) 372vs
$W(CO)_5$Metrz	2077w 1928vs 1900vs	592(sh) 585vs	548m	480(sh)	432(sh)	412m	370vs
$Cr(CO)_5$Phtrz	2071w 1937vs 1903vs	672vs 660vs	551m	448(sh) 438s	410m	380w	
$Cr(CO)_5$Metrz	2070w 1931vs 1900s	652vs	550m	440s	312m		

s = strong, m = medium, w = weak, v = very, sh = shoulder.

[a] Recorded in toluene. [b] Recorded as KBr disc.

Vibrational spectra of a number of 1,2,4-triazole complexes have been reported recently [4]. In many cases information about the nature of the coordination could be obtained from the vibrations observed between 500 and 700 cm^{-1}. For methyl- and phenyl-triazoles there are complications in this approach because methyl and phenyl vibrations strongly influence the spectrum in this region. As a result, little can be said with certainty about the effect of coordination on the vibrational spectra of these ligands. The vibrations between 500 and 700 cm^{-1} have been listed in Table 3 and the bands have been assigned according to the literature [9,10]. Table 3 shows that little difference is observed between the spectra of the free and coordinated Phtrz. The differences are more substantial for the Mertz complexes but no conclusive structural information can be derived. No bands which can be assigned to metal—nitrogen vibrations were observed, and this would indicate that they occur at energies below 250 cm^{-1}, as in the case of the corresponding pyrazole complexes [3].

Proton magnetic resonance spectroscopy

^{1}H NMR has proved to be useful in determining the nature of the coordination of the triazole ligands in the complexes reported here. For a monodentate coordination, the equivalence of the triazole protons, observed in the spectrum of the free ligand, is removed and these protons appear as a pair of singlets. The ^{1}H NMR spectra were obtained in a number of solvents including toluene-d_8, benzene-d_6, acetone-d_6, methanol-d_4 and CDCl$_3$. The results are outlined in Tables 4 and 5. The spectra clearly suggest a monodentate coordination for the triazole ligands. Both Phtrz complexes show different spectra in the various solvents. These spectral differences are not as great for the free ligand.

In methanol-d_4 solution the spectra of the Phtrz complexes consist of a pair of singlets, which are assigned to the triazole protons, and a poorly resolved multiplet, which can be assigned to the phenyl protons. More complex spectra were obtained in benzene-d_6 and toluene-d_8 (see Table 5) and the spectra of W(CO)$_5$Phtrz in methanol-d_4 and toluene-d_8 are compared in Fig. 3. The influence of the solvent on the spectra is best illustrated by examining the spectra obtained for W(CO)$_5$Phtrz in perdeuterotoluene in the presence of varying quantities of methanol-d_4. Figure 4 shows that the addition of perdeutero-

TABLE 3

INFRARED SPECTRA OF THE 1,2,4-TRIAZOLES BETWEEN 700 and 500 cm^{-1}

Compound	Ph ring vibration	Triazole ring def.	ν(N—CH$_3$)	Triazole ring def.	Ph ring vibration	Ph ring vibration
W(CO)$_5$Phtrz	680m	690s	—	640m	610mw	517m
Cr(CO)$_5$Phtrz	682(sh)	691s	—	640m	610mw	518m
Phtrz	687s, 674w	696m	—	642m	612vw	533m
W(CO)$_5$Metrz	—	685m	678m	630vs	—	—
Cr(CO)$_5$Metrz	—	689m	665(sh)	628s	—	—
Metrz	—	682vvw	671m	628vs	—	—

s = strong, m = medium, w = weak, v = very, sh = shoulder.

TABLE 4

PROTON NMR PEAK POSITIONS FOR THE TRIAZOLE COMPLEXES IN DEUTEROMETHANOL (in ppm)

Compound	Triazole	Phenyl	methyl
$W(CO)_5Phtrz$	9.14 (1H, s) 8.89 (1H, s)	7.62—7.60 (5H, m)	—
$Cr(CO)_5Phtrz$	9.16 (1H, s) 8.83 (1H, s)	7.55 (5H, s)	—
Phtrz	8.96 (2H, s)	7.59—7.57 (5H, m)	—
$W(CO)_5Metrz$	8.83 (1H, s) 8.35 (1H, s)	—	3.77 (3H, s)
$Cr(CO)_5Metrz$	8.56 (1H, s) 8.29 (1H, s)	—	3.69 (3H, s)
Metrz	8.50 (2H, s)	—	3.85 (3H, s)

methanol causes a change in the spectrum. It is seen that the two triazole protons are most affected and this can be explained by hydrogen bonding of the free nitrogen in the triazole ring to the protic solvent. Such a protonation effect is also observed in the NMR spectra of pyrazoles [11] and other heterocyclic compounds [12]. Hydrogen bonding will reduce the electron density in the triazole ring and therefore deshield the triazole protons. Further evidence for hydrogen bonding is obtained by examining the shape of the hydroxyl peak of the perdeuteromethanol. At 30% (v/v) methanol-d_4 this peak is broadened as are the triazole proton resonances. On increasing the CD_3OD concentration in toluene-d_8 sharp peaks are obtained again, presumably because of a fast exchange between the hydrogen bonding molecules.

The reason for the complicated phenyl pattern obtained for the Phtrz complexes in aromatic solvents might be explained by a strong interaction between the solvent and the solute. It has been shown previously that aromatic solvents like benzene and toluene can greatly influence the NMR spectra of polar solutes [12,13]. Although no definitive explanation for these aromatic solvent induced shifts (ASIS) has been presented, a number of possible mechanisms have been proposed. It seems likely that a dipole—dipole interaction is

TABLE 5

PROTON NMR PEAK POSITIONS OF THE Phtrz COMPLEXES IN VARIOUS SOLVENTS (in ppm)

Compound	Triazole	Phenyl	Solvent
$W(CO)_5Phtrz$	9.14 (1H, s), 8.89 (1H, s)	7.62—7.60 (5H, m)	CD_3OD
	8.66 (1H, s), 8.34 (1H, s)	7.71—7.35 (6H, m)	$CDCl_3$
	7.17 (1H, s), 6.74 (1H, s)	5.92—5.64 (5H, m)	$(CD_3)_2CO$
	7.46 (1H, s), 6.96 (1H, s)	6.84—6.76 (3H, m), 6.03—5.90 (2H, m)	C_6D_6
	7.57 (1H, s), 7.03 (1H, s)	6.95—6.73 (3H, m), 5.99—5.91 (2H, m)	$C_6D_5CD_3$
$Cr(CO)_5Phtrz$	9.16 (1H, s), 8.83 (1H, s)	7.55 (5H, s)	CD_3OD
	8.50 (1H, s), 8.34 (1H, s)	7.63—7.31 (5H, m)	$CDCl_3$
	7.42 (1H, s), 7.05 (1H, s)	6.90—6.61 (3H, m), 5.97—5.81 (2H, m)	C_6D_6
	7.50 (1H, s) [a]	6.97—6.83 (3H, m), 5.89—5.79 (2H, m)	$C_6D_5CD_3$
Phtrz	8.96 (2H, s)	7.59—7.57 (5H, m)	CD_3OD
	8.82 (2H, s)	7.75—7.44 (5H, m)	$(CD_3)_2CO$
	8.50 (2H, s)	7.53—7.41 (5H, m)	$CDCl_3$
	7.81 (2H, s)	7.11—6.86 (3H, m), 6.62—6.49 (2H, m)	$C_6D_5CD_3$
	7.92 (2H, s)	6.70—6.81 (3H, m), 6.63—6.51 (2H, m)	C_5D_6

[a] Other triazole proton obscured by solvent peaks. s = singlet, m = multiplet.

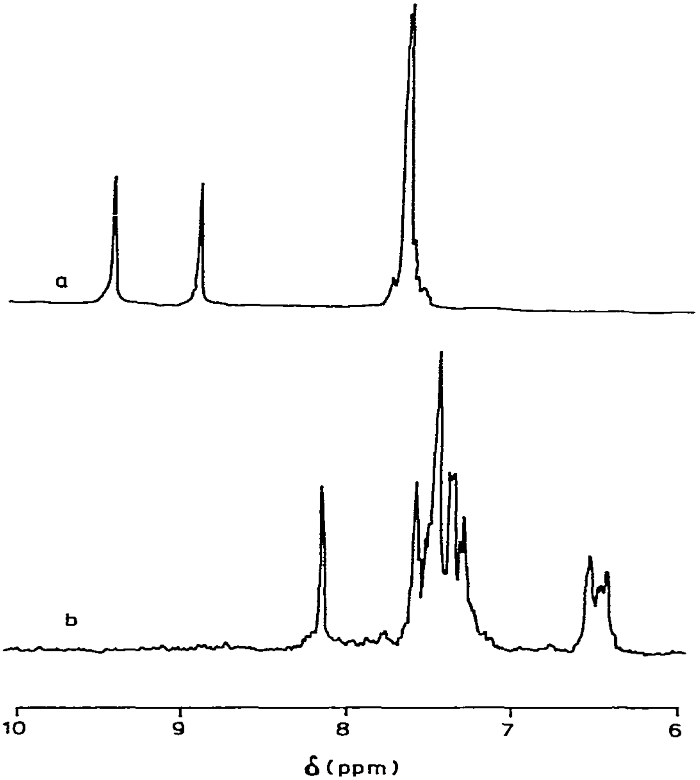


Fig. 3. The ^{1}H NMR spectrum of W(CO)$_5$Phtrz in (a) methanol-d_4 and (b) in toluene-d_8 at room temperature.

the main reason for the phenomenon. A coordination of solvent molecules to the solute has been proposed, but whether this coordination is on a 1 : 1 basis or in the form of a time averaged collision complex is a matter of debate [13]. Laszlo [13] proposed that the aromatic solvent interacts with the electron deficient part of a solute molecule, effectively shielding the protons in this region.

Because of the dipolar character of the interactions, heterocyclic molecules often show ASIS and pyridines and pyrazoles are known for their ability to interact with aromatic solvents [11,14]. ^{1}H NMR spectra of a number of pyrazoles, tetrazoles and triazoles in different solvents have been discussed in the literature [14,15].

An ASIS type interaction between the aromatic solvent and the triazole complexes might be used as an explanation for the shifts observed in the spectra of the complexes reported here. Although these shifts are observed for both the Phtrz and the Metrz complexes, it is more difficult to differentiate between solvent shifts and an ASIS type phenomenon in the Metrz complexes. The existence of ASIS is made evident in the Phtrz compounds by a specific shielding of two of the phenyl protons.

The protons in the Phtrz complexes which are most affected by the presence

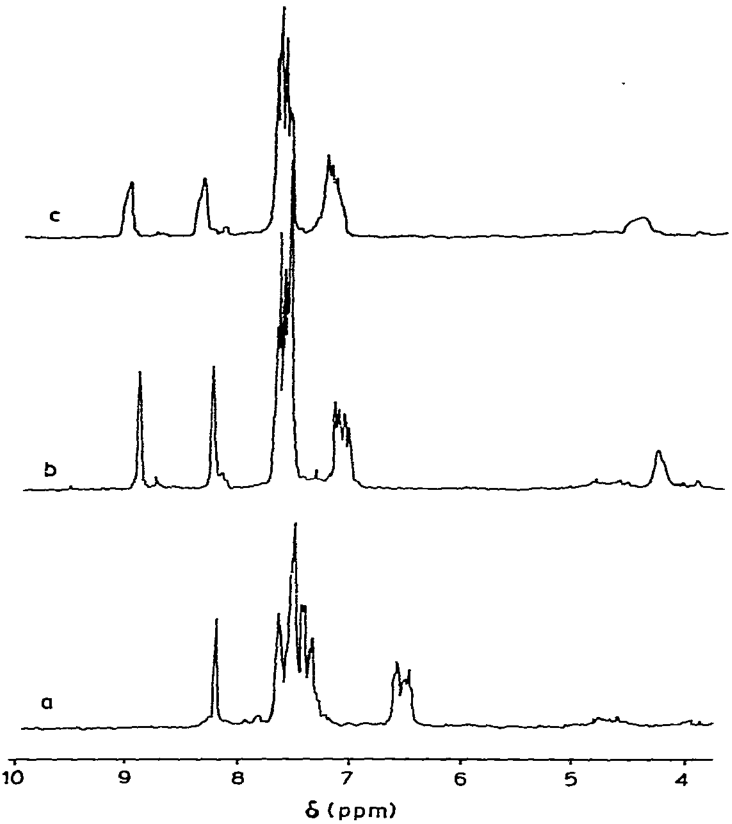


Fig. 4. The ^{1}H NMR spectrum of W(CO)$_5$Phtrz in (a) pure toluene-d_8, (b) 20% (v/v) methanol-d_4 in toluene-d_8. (c) 30% (v/v) methanol-d_4 in toluene-d_8.

of an aromatic solvent are the triazole ring protons and two protons of the phenyl ring. The localised nature of the ASIS would support the suggestion that the phenyl protons most affected would be those which are close to the triazole ring. We therefore assign the multiplet which is shifted upfield in aromatic solvents to the 7 and 11 protons.

The shielding of these protons seems to suggest that the interaction of the solvent molecules with the complex is strongest in the region of the phenyl—triazole ring bond (see Fig. 5). The affect of aromatic solvents on the spectra of the free ligand is less than that observed for the metal complexes. This would suggest that the σ-donation of the ligand to the metal causes a polarisation of the ligand and results in a more electron deficient nitrogen in the 4-position.

These solvent—solute interactions are expected to be stronger at lower temperatures and therefore we have measured the temperature dependence of the ^{1}H NMR spectrum of W(CO)$_5$Phtzr between −80 and 90°C in toluene-d_8 and between 22 and 60°C in methanol-d_4. In CD$_3$OD little temperature dependence was observed. In C$_6$D$_5$CD$_3$, however, a shift of the triazole protons and of the 7 and 11 protons occurs. Figure 6 shows that on lowering the temperature, these protons shift towards higher field whereas the other phenyl protons are

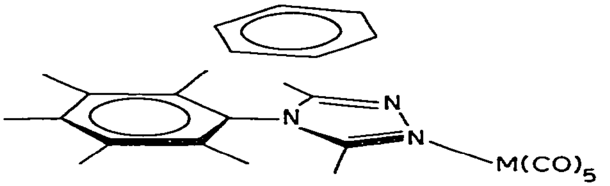


Fig. 5. Interaction of aromatic solvents with metal carbonyl triazole complexes.

unaffected. These observations support a solvent—solute interaction centered at the 4-nitrogen.

It is interesting to compare the triazole complexes with some similar pentacarbonyl complexes with diazenes recently reported by Frazier and Kisch [16]. The strong difference in π-back-bonding capacity between the two types of nitrogen donor ligands lead to a number of striking differences in behaviour. In the diazene complexes a low lying π^* orbital is available for back-donation from the metal to the ligand. This gives rise to a rapid shuttling of the metal—ligand bond between the two nitrogen atoms. This shuttling is observed at temperatures as low as —40°C. For the triazole complexes, however, we find a stable coordination to one of the nitrogens up to temperatures as high as

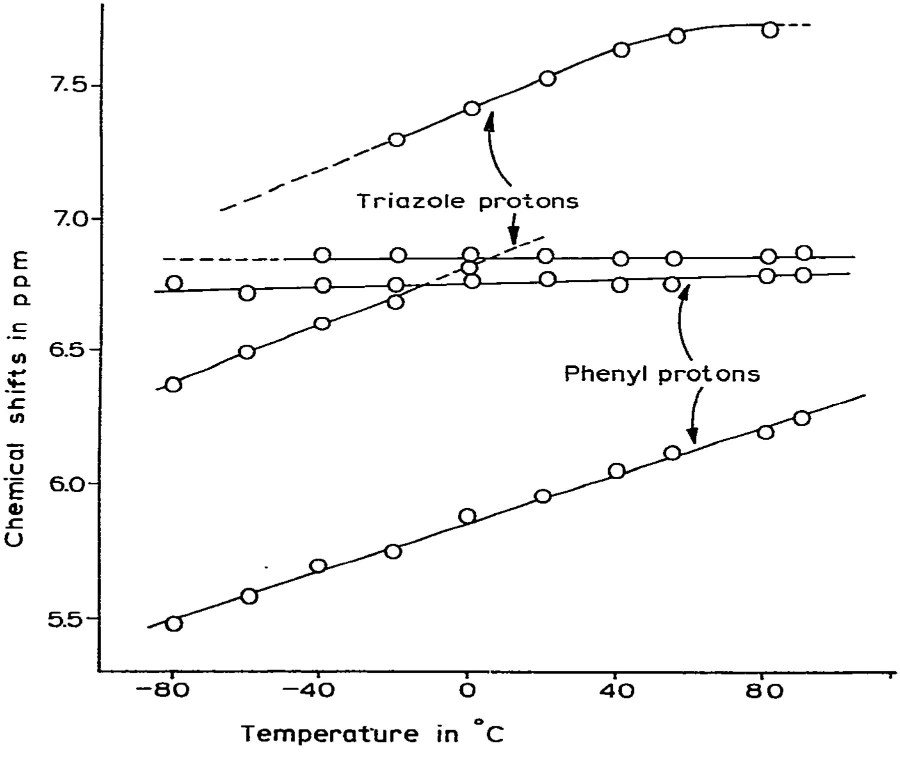


Fig. 6. Plot of the temperature dependence of the proton NMR spectrum of $W(CO)_5Phtrz$ in toluene-d_8. Solvent resonances occur between 7.0 and 7.1 ppm.

80°C. This difference in behaviour can be explained by the absence of low-lying π^* orbitals in the triazole ligand, and it is assumed that the activation energy for a rapid shuttling is higher in the case of a simple σ-bond.

The existence of π-back-donation to the N=N bond in the diazene ligand gives the metal to ligand bond some double bond character and Frazier and Kisch [16] observed a restricted rotation around the metal to ligand bond. In complexes with ligands capable of strong back-bonding, there are two preferred orientations of the uncoordinated nitrogen atom. In the first orientation the free nitrogen is located between the two equatorial carbonyl groups. This orientation is expected to have the lowest energy as steric interactions are minimised. In the second orientation the uncoordinated nitrogen is located in the M—C—O plane. The destabilising affect of the steric interaction between the nitrogen and the carbonyls is thought to be balanced by a better overlap of the orbitals which are effective in the back-bonding process. As in our case little or no back-bonding is taking place, the first orientation should be favoured. It is interesting to note that this orientation is indeed observed in the crystal structure of the $W(CO)_5$Phtrz complex [17].

Conclusion

$W(CO)_5$ and $Cr(CO)_5$ complexes of 4-phenyl-1,2,4-triazole and 4-methyl-1,2,4-triazole have been prepared in which the N-donor acts as a monodentate ligand. It has been shown that ^1H NMR spectroscopy is useful in determining the nature of the coordination of these ligands. The ^1H NMR spectra show that strong interaction occurs between the solute and solvent molecules in aromatic solvents. The σ-donation of the ligand to the metal appears to increase the strength of this interaction.

Experimental

Materials

The metal hexacarbonyls were obtained from Strem Chemicals and used without further purification. 4-Phenyl-1,2,4-triazole and 4-methyl-1,2,4-triazole were prepared as described by Bayer [18,19] using CH_3NH_2, $C_6H_5NH_2$ and formylhydrazine as starting materials. Absolute alcohol was obtained from Merck and used without further purification. NMR solvents were obtained from Merck and Fluorochem.

Preparation of $W(CO)_5$Phtrz, $Cr(CO)_5$Phtrz, $W(CO)_5$Metrz and $Cr(CO)_5$Metrz

All compounds were prepared by the same route involving initial photolysis of the hexacarbonyl (conc. 1.5×10^{-2} *M*) in ethanol suspension for approximately 8 hours to form the $M(CO)_5EtOH$ adduct. A mole equivalent of the ligand was then added to this solution and the solvent removed under reduced pressure at room temperature. The crude products were then purified by chromatography on neutral alumina using acetone as eluent. The yellow complexes were further purified by slow crystallisation from acetone/ethanol mixtures.

TABLE 6

ELEMENTAL ANALYSES (%)

Compound	Found			Calculated		
	C	H	N	C	H	N
$W(CO)_5$Phtrz	32.96	1.13	8.98	33.27	1.49	8.95
$Cr(CO)_5$Phtrz	44.98	2.08	12.17	46.29	2.08	12.46
$W(CO)_5$Metrz	22.59	1.22	10.32	23.60	1.23	10.32
$Cr(CO)_5$Metrz	34.72	1.81	15.27	34.91	1.82	15.27

Equipment

Quantum yield determinations were made by ferrioxalate actinometry and are accurate to 10%. Quantitative photolyses were carried out in quartz cells with a path-length of 1 cm. The reactions were monitored by ultraviolet spectroscopy.

Preparative photolyses were carried out in a standard pyrex glass photochemical reactor. The light source was a Phillips HPK 125 W mercury lamp filtered through pyrex glass.

Ultraviolet-visible spectra were obtained on a Pye-Unicam SP8-200 spectrophotometer. Peak positions are accurate to 1 nm and extinction coefficients have an accuracy of 10%. Infrared spectra were obtained on a Perkin-Elmer 599 spectrophotometer. Peak positions are accurate to ± 4 cm^{-1} above 2000 cm^{-1} and to ± 2 cm^{-1} below 2000 cm^{-1}. ^{1}H NMR spectra were obtained on a Brucker WP 80 or a Jeol PS-100; peak positions were measured relative to an internal TMS standard.

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