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Thiazolidine-2-thione Complexes with Group VI B Metal-carbonyls

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By u.v. irradiation of toluene solutions of $[M(CO)_6]$ *and* ttz *the complexes* $[M(CO)_5ttz]$ (*where*: M = *Cr, Mo, W, and ttz = thiazolidine-2-thione*) *were obtained, which are yellow, crystalline, diamagnetic and non-electrolytes. By means of the mass-spectra, i.r. and n.m.r. studies a full characterization of the free ligand and of the complexes was obtained. Full evidence is given that the co-ordination bond takes place through the sulphur atom of thioketonic group. A* S_N1*-type mechanism of the photochemical reactions was pointed out by determining the quantum yields.*

Introduction

We are interested in the problem of the competition between V A and VI A donor atoms in the formation of the co-ordination bond to the metal when the donor atom is one of a sterically hindered ligand. Up to now, we have prepared and characterized many complexes with VI B, VIII, I B, and II B group metals using ligand molecules with three different reaction centres, like thiomorpholin-3-one ($S-CH_2-CH_2-NH-CO-CH_2$ = *tm*) and thiazolidine-2-thione ($S=C-NH-CH_2-CH_2-S$ = *ttz*).[1-8] In particular we recently reported the complexes with *tm* of group VI B metal-carbonyls, having general formula *cis*–$[M(CO)_4tm_2]$ (where: M = Cr, Mo, W).[5] In these compounds the ligand seems bonded to the metal through the sulphur atom.

We have now obtained, by u.v. irradiation of a deoxygenated toluene solution of $[M(CO)_6]$ and *ttz*, in molar ratio from 1:1 to 1:4, the complexes $[M(CO)_5ttz]$ which are yellow and crystalline.

The protochemical reaction was studied thoroughly. These compounds are stable for a long time if kept under nitrogen and in a dark place at low temperature; the stability decreases in the order Cr ≫ W > Mo. These compounds are also obtainable, but in lower yield, by thermal reaction.

In order to characterize these complexes, physico-chemical studies such as conductivity and magnetic susceptibility measurements were carried out. Actually the complexes exhibited a diamagnetic and a non-electrolyte behaviour. Further u.v., i.r., n.m.r. and mass-spectroscopic studies were carried out in order to determine the binding site of the ligand to the metal atom and the number of molecules involved in the formation of the complex.

Some analytical results and physical properties are reported in Table I.

Spectroscopic results on the structural characterization of the complexes. In the mass spectra the most intense peak is due to the parent ion $[M(CO)_5ttz]^+$. Furthermore we have found five more peaks with Δ-mass of 28 a.m.u., the last one being due to $[Mttz]^+$ ion, confirming thus the presence of five carbonylic groups.

The main characteristics of the electronic spectra are shown in Figure 1. These results will be used in the kinetic study. The i.r. spectra have been recorded over the range 4000-200 cm^{-1}; the assignments of

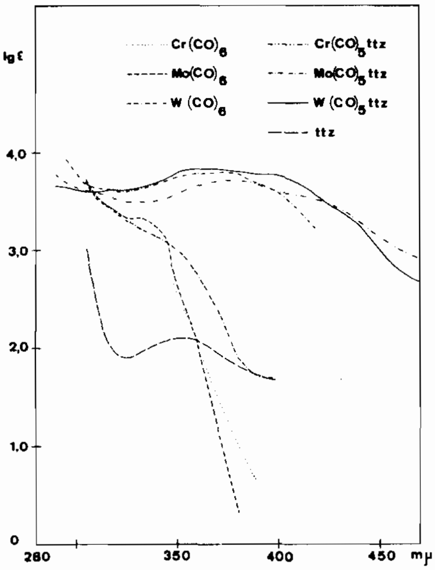

Figure 1. Electronic spectra of reagents and compounds.

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Table I. Analyitical data and some physical properties.

Compound	Colour	Dec.p.°C	Stability	Found mw	Found M	Found C	Found H	Required mw	Required M	Required C	Required H
[$Cr(CO)_5ttz$]	Yellow	77-78	V.St.	311	16.8	30.8	1.6	311.26	16.7	30.9	1.6
[$Mo(CO)_5ttz$]	Yellow	70	Unst.	—	27.4	27.3	1.7	355.20	27.0	27.1	1.4
[$W(CO)_5ttz$]	Yellow	78	St.	440	41.5	21.5	1.2	443.11	41.5	21.7	1.1

All compounds are diamagnetic and non-electrolytes in chloroform solutions; were prepared by U.V. irradiation of toluene or ethyl ether solutions (with molar ratios from 1:1 to 1:4) and purified by TLC technique; are very soluble in toluene, chloroform, ethyl- or n-buthyl ether.

Table II. Assignments of infrared bands (KBr discs).

ref. 9	ttz	[$Cr(CO)_5ttz$]	[$Mo(CO)_5ttz$]	[$W(CO)_5ttz$]
ν(N—H)	3400 [a]; 3120s	3400m	3400m	3400m [a]
ν(CO)		2062w; 1985w 1942s ; 1910sh	2085vw; 1985vs 1945ms ; 1890sh	2070w; 1980vs 1938s ; 1885sh
Thioamide I	1490s	1518s	1515s	1505s
Thioamide II		1350w	1350vw	1355vw
ν(C=S)+δ(NCS)	1288vs	1300s	1298s	1310ms
ν(C—N)	1035m	1052s	1052s	1052s
ν(CH_3)+ν(CN)+ν(CS)	993m	1000s	1000s	1000s
Thioamide III	928ms	935s	935s	935m
ν(C—S)$_{sym}$	690vs	698m	698m	695m
ν(C—S)$_{antisym}$	650vs	655s	655s	655ms
δ(NCS)	578m	585m	589vs	585vs
η(CC′)	540m	544m	545w	545mw
ν(CN)+δ(CNC)	434s	436ms	435m	435mw
		370s	370s	372vs
ν(NCS)+δ(CNC)	290m	291mw	291vw	291vw

[a] in chloroform solution.

Table III. Chemical shift values in p.p.m. from TMS for deutero-chloroform solutions of free ligand and complexes.

	δNH	δCH_2(4)	δCH_2(5)	δν_{AB}
ttz	8.21±.03	4.01±.01	3.58±.01	0.43
[$Cr(CO)_5ttz$]	7.35 »	4.13 »	3.65 »	0.48
[$Mo(CO)_5ttz$]	7.51 »	4.15 »	3.68 »	0.47
[$W(CO)_5ttz$]	7.52 »	4.18 »	3.69 »	0.49

the principal infrared absorption bands are reported in Table II, according to Singh *et al.*[9]

Much information is available in the literature about V A group donor atoms in [$M(CO)_5L$] complexes[10-21] whereas only limited data for ligands of VI A group are reported.[15,18] Neverthless, it is well known[22-24] that the CO stretching bands are shifted towards higher frequencies in sulphur-bonded complexes than in N—, P—, or As—bonded ones. In the present case we observe that the B_1 and E modes, the most intense bands, fall at higher wave numbers than found by Cotton[24] for similar N—bonded complexes with heterocyclic ligands.

This fact supports the hypothesis that, in our compounds, the ligand is bonded to the metal through one sulphur atom. Further support for this hypothesis is given by the position of the N—H stretching band of the three complexes which falls at the same wave number as in the spectra of the free ligand in chloroform solution. The solid phase i.r. spectra are complicated by intermolecular interactions and are therefore not available for an empirical discussion. Thus, the small positive shifts (of about 5-10 cm^{-1}) of thioamide I band present in solid phase spectra and of the bands ν(C=S)+δ(NCS) and ν(C—S) symmetric and antisymmetric, are not very significant. On the other hand, when the co-ordination bond involves the nitrogen atom of thiazolidine-2-thione (as in Zn— and Cd—derivatives[8]) the ν(N—H) band is shifted towards low frequencies by about 300 cm^{-1}, while the thioamide I band and ν(C=S)+δ(NCS) show positive shifts of about 40 and 20 cm^{-1} respectively.

The n.m.r. spectrum of the free ligand shows a broad peak at 8.21 p.p.m. (TMS as internal standard),

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clearly due to the proton resonance of the NH group. In the range between 3.5 and 4.15 p.p.m. we observe two different groups of peaks. This system can be assigned to the AA'BB'-part of an AA'BB'X-system, suggesting the proton resonances of the $-CH_2-CH_2-NH-$ fragment, where the X-part is the NH-proton resonance. On D_2O addition the 8.21 peak disappeared corresponding to complete exchange, while the remaining part of the spectrum became an AA'BB'-system, confirming this hypothesis.

The assignments of CH_2–proton resonances was made on the basis of the line-shape modification caused by exchange decoupling process (for chemical shift values see Table III).

The NH–deuterated thiazolidine-2-thione spectrum is a « deceptively simple » one with seven transitions *per* group, i.e. 14 transitions in all. Usually a seven-line spectrum, such as that of 1.2-disubstituted ethanes, is not completely analysable to an unequivocal solution[25] but, in our case, this difficulty has been overcome by comparing the 100 MHz with the 60 MHz spectrum. In the 60 MHz spectrum we observe the 7- and 7'-lines, according to Pople's nomenclature,[26] which are not detectable at 100 MHz because of lower intensity. In this way we have been able to carry out a full analysis of the AA'BB'X–system obtaining the following values for the relative parameters: $K = 23.6$; $M = 0$; $N = 15.9$; $L = 1.2$; $\delta\nu_{AB} = 0.43$ p.p.m. From these parameters J–values typical of 5-member heterocyclic-saturated molecules are obtained; 8.55 and 7.35 Hz for the vicinal J–values and 11.8 Hz for both geminal J–values.[27] In particular the vicinal J–values suggest a non-rigid structure.[28]

As far as the coupling between the NH and $CH_2(4)$ protons in $-CH_2(4)-NH-$ fragment is concerned, theoretical analysis of the spectra shows that both J–values are about the same and exhibit the value $1.2 \rightarrow 1.5$ Hz. This evaluation cannot be more accurate because of quadrupole moment and exchange broadening of the resonances.

On passing from the free ligand n.m.r. spectrum to the spectra of just purified complexes (by TLC method) we first notice that AA'BB'X–systems are again present without sensible variations in the values of the spectral parameters K, L, M, N.

Furthermore, from Table III one observes that: (1) the chemical shift values of the NH proton fall at about 0.8 p.p.m. to higher fields than in the free ligands*; (2) the chemical shift values for both CH_2 proton resonances are slightly shifted towards lower fields than those of the free ligand; (3) on passing from Cr- to W-derivatives the deshielding effect of about 0.17 p.p.m. is also noticeable on the NH proton resonance; (4) both CH_2 resonances exhibit slight shifts to lower field of about the same value (0.04 p.p.m.) on going from Cr- to W-derivatives, and further the evaluated shift between $CH_2(4)$ and $CH_2(5)$ resonances ($\delta\nu_{AB}$) is practically constant in all complexes.

From the i.r. and n.m.r. results it is possible to obtain an unequivocal characterization of these complexes with regard to the atoms involved in the metal-ligand bond.

In fact, the comparison between the wave numbers of ν(NH), in the free ligand and in the complexes supports the hypothesis that the co-ordination bond does not take through the nitrogen atom. This hypothesis is also supported by the shift towards higher frequencies of the ν(CO), typical of S-bonded pentacarbonyl-derivatives.[22-24] Thus the ligand should be bonded to the metal through one of the sulphur atoms, as in models A and B of Figure 2.

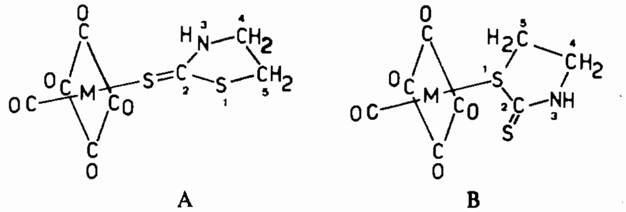

Figure 2. Scheme of possible isomers in the co-ordination bond through the sulphur atoms of $[M(CO)_5ttz]$.

The n.m.r. data also support the hypothesis that the nitrogen atom is not involved in the metal-ligand bond and seem consistent only with model A of Figure 2.

In fact, in the model A the $CH_2(4)$ and $CH_2(5)$ protons would be magnetically equivalent with respect to the CO-dipole system if we assume that the ligand molecule is freely rotating around the M–S bond. This equivalence would not be found neither in model B of Figure 2 nor with a co-ordination bond through the nitrogen atom.

From Table III we observe first that in the formation of all complexes both CH_2 resonances exhibit a shift of the same sign and value, meaning that both shielding constants are equally affected by the co-ordination. Further the shift between $CH_2(4)$ and $CH_2(5)$ resonances, that is $\delta\nu_{AB}$, is maintained practically constant on going from the Cr- to W-complexes. These results support a rather symmetric position of the two CH_2-groups with respect to the strongly anisotropic carbonyl plane. If, as in the B-hypothesis, an asymmetric CH_2 position with respect to the carbonyls plane is postulated, the $\delta\nu_{AB}$ should be detectably affected on going from Cr- to W-derivatives, as a consequence of the lengthening of the metal-ligand bond. On the other hand the same conclusion is supported by the invariance of the spectral parameters, K, L, M, N in our materials. Moreover, model B of Figure 2 would call for a behaviour of NH and CH_2 (5) resonances more similar than that actually occurring.

Other characteristics of the n.m.r. spectra are a rather large shielding effect of the NH resonance and a rather small deshielding effect on both CH_2 resonances as a result of the co-ordination (see Table III).

(*) This result has been obtained by comparing the spectra of solutions of the free ligand and of complex of about the same concentrations. On the other hand we observe that the chemical shift value of NH-resonance in the free ligand spectrum is concentration-dependent, moving towards higher fields by dilution of about 0.5 p.p.m.

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At the moment, no consistent explanation for these opposite effects can be presented, given the lack of n.m.r. data on these systems and the strong magnetic anisotropies presented by the carbonyl plane, the heavy metal atom and the sulphur atoms in the ring.

It would appear that two opposite effects come into play, one strong shielding effect at shorter range —due to carbonyl anisotropy—acting only on the closer NH proton, plus a weak deshielding effect too small to be assigned to any specific cause, which seems also correlated with the length of the metal-sulphur bond. However, this feature of the spectra does not interfere with the conclusions drawn above. More n.m.r. work needs to be done in these systems before these effects might be fully understood.

We therefore conclude that the *ttz* molecule is bonded to the metal through a sulphur atom, probably the thioketonic one. This conclusion is consistent with Ahrland's classification[29] and with the fact that this atom is the less sterically hindered donor atom in our ligand.

Photochemical reactions mechanism. The kinetic mechanism of the photochemical reaction has been studied using spectrophotometric techniques.

As show in Figure 1, the electronic spectra of our complexes show in the range from 350 to 450 mμ a peak accompanied by a shoulder. Unfortunately, it is not convenient to use the wave length of the peak to measure the product concentration because at this value the absorption of the reagent solutions is considerable. Therefore, we have chosen for our measuremens the wave length of 394 mμ, near the shoulder, where the spectra show a low slope and at which value the solutions of both reagents present a very small absorption (a correction of 0.04 to the absorbance value has been used, for the runs a–g (see Table IV); no correction was necessary for more diluted runs (h–s)). The molar absorbance of the products at 394 mμ is 4350, 4500, and 5500 for Cr-, Mo-, and W-derivatives respectively.

All the photochemical experiments have been carried out under pseudo first order conditions, using alternatively a large excess concentration of ligand or of metal-carbonyl (see Table IV). Samples of a stock solution, kept in a dark place and at low temperature, have been irradiated with 366 mμ light for different times. The absorbance values, recorded at 394 mμ, have been plotted against the net time of exposure in Figure 3.

Because the concentration of the reactants decreases with time whereas increases that of the complex which absorb at 366 mμ too, the three reactions quantum yields at the zero time have been evaluated. Several $\varphi_{app.}$ values have been determined at different times for each run (see experimental). Plotting log $\varphi_{app.}$ against log (t+1) (see Figure 4)[30] we have obtained the φ values at zero time reported in Table IV. For the chromium reaction a value of 1.00±0.05 as predicted for a S_N1 mechanism[31] has been obtained in every run while for tungsten and molybdenum reactions the value so calculated are lower than 1.00. Values lower than 1.00 have usually been obtained for bisubstitution reactions. No bisubstituted products have been observed in our experiments even working with a large ligand excess.

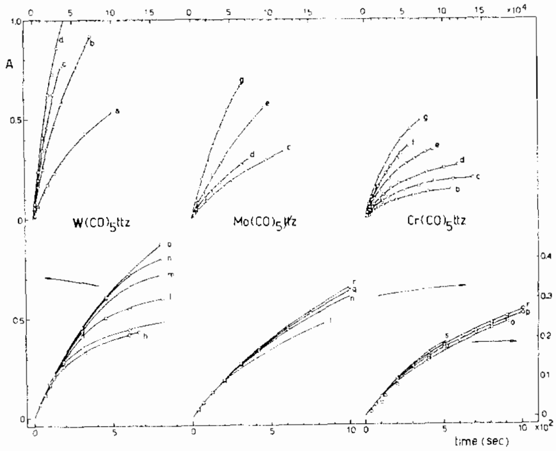

Figure 3. In the top of the graph [ttz] = 4.10^{-2} *M* and $[M(CO)_6]$ ranging from 2 to 8.10^{-4} *M;* in the bottom $[M(CO)_6]$ = 1.6 10^{-3} *M* and [ttz] ranging from 2.5 10^{-5} to 1.5 10^{-4} *M*. For codes see Table IV.

The low φ values for W- and Mo-derivatives could be explained on the basis of a different mechanism or a decomposition process of $[Mo(CO)_5ttz]$ and $[W(CO)_5ttz]$. In fact, as above reported, these complexes are much less stable than the chromium one.

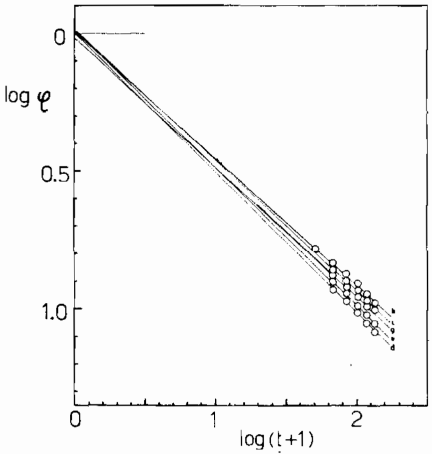

Figure 4. Extrapolation of φ value at zero time for chromium runs.

In order to check for a different mechanism in the molybdenum and tungsten reactions, the apparent rates at zero time have been evaluated from the experimental data by means of an equation of the type

$$A=\alpha+\beta t+\gamma t^2+\delta t^3+\ .....$$

where A is the absorbance and t the time. The poly-

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Table IV. Logarithms of apparent initial rates (moles $l^{-1}sec^{-1}$) (*), fraction of light absorbed and quantum yield (at t=0) for the photochemical reactions (measurements at 394 mμ and irradiation at 366 mμ).

$[ttz]_0=4.10^{-2}M$ Code	$\log[M(CO)_6]_0$	Tungsten log v_0	Tungsten f	Tungsten φ_{app}	Molibdenum log v_0	Molibdenum f	Molibdenum φ_{app}	Chromium log v_0	Chromium f	Chromium φ_{app}
a	−3.699	−7.708	0.179	0.9_2						
b	−3.398	−7.406	0.279	0.8_6				−8.132	0.074	1.0_2
c	−3.222	−7.213	0.366		−7.950	0.107	0.7_6	−8.018	0.107	1.0_4
d	−3.097	−7.126	0.444	0.8_1	−7.803	0.137	0.6_0	−7.864	0.169	1.0_1
e	−2.921				−7.671	0.193		−7.704	0.227	1.0_5
f	−2.796									
g	−2.699				−7.429	0.295	0.7_7	−7.494	0.331	0.9_5
B(**)		−4.055			−4.814			−7.951		
n(**)		0.986			0.971			0.942		
$[M(CO)_6]_0=1.6\ 10^{-3}M$ Code	$\log[ttz]_0$	log v_0			log v_0			log v_0		
h	−4.602	−6.532								
i	−4.301	−6.466								
l	−4.125	−6.450			−6.899					
m	−4.000	−6.484								
n	−3.903	−6.489			−6.943					
o	−3.824	−6.493						−6.921		
p	−3.699							−6.978		
q	−3.523				−6.951			−6.896		
r	−3.398				−6.940			−6.975		
s	−3.301							−6.965		
B(**)		−6.327			−7.129			−7.138		
n(**)		0.038			0.052			0.054		

(*) $v_o = \beta/\varepsilon_{394}$ where $A=\alpha+\beta t+\gamma t^2+\delta t^3$. (**) from the equation $\log v_o=B+n \log C$.

nomial has been truncated after the third power of the time.*

In Figure 4 log v_o ($v_o = \beta/\varepsilon$ where ε is the molar absorbance) are plotted against the logarithm of the initial concentrations of the reagent. The slopes of the straight lines** are 1.00±0.05 with respect to metal-carbonyl and 0.00±0.05 with respect to the thiazolidine-2-thione. These results clearly confirm that the same S_N1 mechanism rules the three reactions and that the anomalous φ values can be attributed to a decomposition process, as in the following scheme

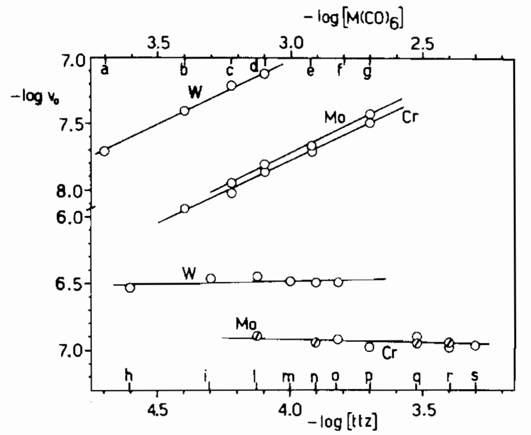

Figure 5. Correlation between the logarithms of apparent initial rates (v_o) and the logarithms of concentrations of reactions.

$$M(CO)_6+h\nu\rightarrow M(CO)_6^*$$

$$M(CO)_6^*\rightarrow M(CO)_5+CO$$

$$M(CO)_5+ttz\rightarrow M(CO)_5ttz$$

$$M(CO)_5ttz\rightarrow \text{dec. products}$$

In the presence of a ligand large excess the back reaction

$$M(CO)_5+CO\rightarrow M(CO)_6$$

can be considered negligible.[30]

Experimental Section

Purification of thiazolidine-2-thione. The ligand, supplied by Fluka, was purified by double recrystallization from hot water (m.p. 106-107°; lit.[32] 106-107°).

Preparation of compounds. The $[M(CO)_5ttz]$ complexes (where M = Cr, Mo, W) were obtained from a deoxygenated toluene solution, under nitrogen atmosphere, of metal-hexacarbonyl and thiazolidine-2-thione in molar ratios from 1:1 to 1:4. After irradiation by u.v. source (about 2 hrs) the solution was yellow. The compound separated out on evaporation of the solvent and it was purified by means of TLC on Merk HF_{254} silica gel plates using benzene as eluent, and crystallized at low temperature in a dark place from an ethyl ether/ligroin mixture (for analytical data, see Table I).

(*) Equations with higher order terms give to curves without physical significance whereas with a second order equation the experimental data are not well reproduced; with our approximation the calculated absorbance values correspond within ± 0.03 to the experimental data.

(**) In every case the straight lines have been evaluated by the least square method.

(32) Handbook of Chemistry and Physics, 48th ed., 1968-69, p. C565.

Mass-spectra. The molecular weight of the complexes were determined by mass-spectroscopic measurements, using a «Atlas Werke CH4» spectrometer. The ionization of the compounds was obtained first at room temperature and then at 60°C, by an accelerated electron beam, with 50 e.V. energy. This value is recommended for spectra of organometallic compounds.[33] The accuracy of the measurements is ± 0.5 a.m.u. The spectra showed the peaks due to the ions: $[M(CO)_5ttz]^+$, $[M(CO)_4ttz]^+$, $[M(CO)_3ttz]^+$, $[M(CO)_2ttz]^+$, $[M(CO)ttz]^+$, $[Mttz]^+$.

Conductivity measurements. These measurements, carried out with a Tinsley, 4896 type electrolytic conductivity bridge in about 10^{-3} *M* chloroform solutions, demonstrated that $[M(CO)_5ttz]$ complexes are non-electrolytes.

Magnetic susceptibility measurements. The measurements were carried out by Gouy's method at room temperature, using Pascal's constants for diamagnetism of the component atoms. The compounds were diamagnetic.

I.R. measurements. All compounds were examined in the region 4000-200 cm^{-1} with Perkin-Elmer models 457 and 225 spectrophotometers. Atmospheric water was removed from the spectrophotometer housing with dry nitrogen. The spectra were recorded in solid phase as potassium chloride discs or, in the far region, as nujol mulls supported between thin polyethylene sheets. The spectra of the complexes in the regions near 3400 cm^{-1} and between 2000 and 1800 cm^{-1} were studied in chloroform solutions too (for assignments, see Table II).

N.M.R. spectra The n.m.r. were recorded in deutero-chloroform solutions on Varian HA 100 and on Jeol JNM-C-60HL spectrometer at 27° C. The chemical shift values are reported in Table III in p.p.m. from TMS as internal standard. In order to determine the spectral parameters an analysis of the patterns were carried out by means of a LACOON III-modified iterative computer program.

Visible and u.v. spectra A Perkin-Elmer model 402 spectrophotometer was used. Spectra were recorded for toluene or ethyl ether solutions of $[M(CO)_5ttz]$ complexes (concentrations: from 10^{-4} to 10^{-6} *M*) (see Fig. 1).

Kinetic apparatus. The irradiation of the samples for the kinetic measurements of the photochemical reaction was carried out using an apparatus consisting of an u.v. Osram light source (contained in an air-thermostated box) 30 cm distant from the silica-cell containing the sample. The light was made monochromatic by a 366 mμ Eppendorff filter. This filter shows an absorbance value of 0.79 at 366mμ and a value of 1.4 at 342 and 380 mμ. The times were selected by a Synchro-Compur's shutter (precision $>$ 1%). The samples were thermostated by a Lauda K 2RD electronic thermostat with precision of ± 0.02° C. The absorbance measurements, after irradiation, were carried out recording the range between 350 and 430 mμ by a Perkin-Elmer model 402 spectrophotometer and using the value read at 394 mμ with precision of ± 0.01 in absorbance.

Kinetic measurements. All kinetic measurements of the photochemical reaction were carried out at 25° C under pseudo first order conditions, using alternatively a large excess of ligand or metal-carbonyl. The logarithms of the concentrations of the samples are reported in Table IV. In the range 10-40°C the reagents are thermically stable.

Quantum yield determination. The apparent quantum yields at the t time of the three reactions have been calculated by means of the formula

$$\varphi_{app} = \frac{N . V . A}{\varepsilon . I_o{}^i . t . f}$$

where N is the Avogadro's number, V is the irradiated volume (l), A is the absorbance at 394 mμ corrected for the reagents contribution at the t time (sec.), ε is the molar absorbance of the formed product at the same wave length, $I_o{}^i$ is the total flux of the incident light (quanta/sec.) and f is the fraction of $I_o{}^i$ absorbed by $[M(CO)_6]$.

The $I_o{}^i$ value, determined by means of a $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ actinometer,[34] was 7.21×10^{14} quanta/sec.

Because the incident ligth, $I_o{}^i$ is not completely absorbed by our reactant solutions (runs a–s) and part of it is absorbed by the ligand, it was necessary to determine the factor f. This was done by measuring at 366 mμ the transmittance of solutions containing a–h concentrations of metal-carbonyl only.

The experimental $\varphi_{app.}$ values calculated at different times for each run have been extrapolated to zero time by plotting log $\varphi_{app.}$ against log $(t+1)$[30] (see Fig. 4) to obtaine the true φ value.

Processing the data. The absorbance values from kinetic measurements were processed by an our special program of multiple regression set up for a Hewlett-Packard model 9100 B calculator. This program allowed us to obtain the parameters of the equation: $A = \alpha + \beta t + \gamma t^2 + \delta t^3 + \ldots$ where A is the absorbance and t the time. The calculated curves reproduce the experimental data within ± 0.03. The standard errors were used to determine the Student's *t* parameters,[35] for which the order of magnitude was 5—10% for the α parameters and much lower than 1% for all the others (β, γ, and δ). The P factors for the apparent rates at zero time, $v_o = \beta/\varepsilon$ (where ε is the molar absorbance), are much lower than 1% in every case. In fact, by determining the v_o value by means of a statistical method it is possible to minimize the errors rising from a graphical evaluation and due to the experimental errors which are obviously larger in the first part of each curve.

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