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SYNTHESIS AND CHARACTERIZATION OF [ReCl(CO)$_3$(L)] [L = 5,6-DIPHENYL-3-(2-PYRIDYL)-1,2,4-TRIAZINE (dppt) OR 3,5,6-TRI(2-PYRIDYL)-1,2,4-TRIAZINE (tpt)] AND THE BIDENTATE COORDINATION OF THE METALLOLIGAND [ReCl(CO)$_3$(tpt)] TO [M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn; hfac = HEXAFLUOROACETYLACETONATE ION)

J. GRANIFO

Departamento de Ciencias Químicas, Facultad de Ingeniería y Administración,
Universidad de La Frontera, Casilla 54-D, Temuco, Chile

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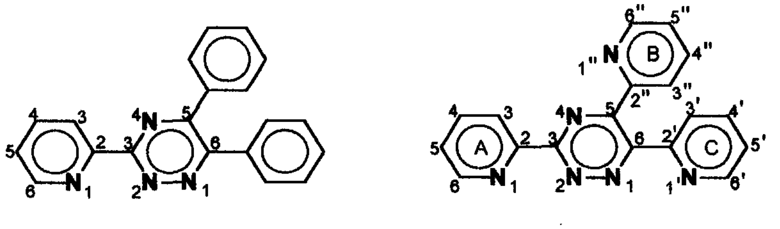
Abstract—The synthesis and characterization of the novel mononuclear species [ReCl(CO)$_3$(L)], where L is 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) or 3,5,6-tri(2-pyridyl)-1,2,4-triazine (tpt), is reported. The coordination mode of the dppt and tpt ligands to the ReCl(CO)$_3$ fragment apparently occurs through a pyridyl nitrogen and a triazine nitrogen. In addition, the tpt based monomer [ReCl(CO)$_3$(tpt)] behaves as a bidentate metalloligand, reacting with the [M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn; hfac = hexafluoroacetylacetonate ion) complexes to produce the heterobimetallic substances [(CO)$_3$ClRe(tpt)M(hfac)$_2$]. In these Re—tpt—M complexes the tpt—M binding is atypical, since only the two free pyridyl nitrogen atoms of the chelating [ReCl(CO)$_3$(tpt)] complex are involved. The new compounds were characterized by IR, ^{1}H NMR and electronic spectroscopy, electrochemical and magnetic moment measurements.

In a previous paper,[1] we reported that the closely related ligands 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) and 3,5,6-tri(2-pyridyl)-1,2,4-triazine (tpt) (Fig. 1) form the mononuclear tetracarbonyl complexes [Mo(CO)$_4$(L)] (L = dppt, tpt). In these complexes the L ligands were considered to be coordinated to the metal centre via the pyridyl N(1) and the triazine N(2) nitrogen atoms. Furthermore, the ligating properties of the [Mo(CO)$_4$(L)] complexes (metalloligand[2] properties) towards the acidic [M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn; hfac = hexafluoroacetylacetonate ion) species were studied. The results demonstrated that only the tpt complex [Mo(CO)$_4$(tpt)] exhibits



dppt

tpt

Fig. 1. Structure of the ligands dppt and tpt.

reactivity to give the binuclear $[(CO)_4Mo(tpt)M(hfac)_2]$ compounds. In these Mo—tpt—M systems, the $[Mo(CO)_4(tpt)]$ complex acts as a bidentate chelating ligand in an unusual mode. More specifically, the tpt—M bond includes no more than the pyridyl nitrogen atoms N(1′) and N(1″) of the metalloligand $[Mo(CO)_4(tpt)]$.

The aim of this work is to extend the above study of the coordination properties of the dppt and tpt ligands by using a new d^6 metal carbonyl fragment. In this regard, we wish to report here the synthesis and characterization of: (a) the novel mononuclear rhenium(I) complexes $[ReCl(CO)_3(L)]$ (L = dppt, tpt) and (b) the heterobimetallic $[(CO)_3ClRe(tpt)M(hfac)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn) compounds obtained by using as precursor the $[ReCl(CO)_3(tpt)]$ complex. Indeed, the chelating behaviour of the precursor complex $[ReCl(CO)_3(tpt)]$ in the Re—tpt—M array is presented in this report as the second example of a tpt-based metalloligand with the uncommon two-pyridyl-nitrogen coordination.

EXPERIMENTAL

Reagent grade solvents were used for all preparations. $[Mn(hfac)_2]\cdot 3H_2O$, $[Co(hfac)_2]\cdot 3H_2O$, $[Ni(hfac)_2]\cdot 3H_2O$ and $[Cu(hfac)_2]\cdot H_2O$ were obtained from the Aldrich Chemical Company. The compounds $[Fe(hfac)_2]$,[3] $[Zn(hfac)_2]\cdot 2H_2O$,[4] dppt[5] and tpt[5] were isolated according to literature methods. IR spectra were registered as solid KBr samples on a Bruker Model IFS-66V FTIR instrument. The electronic spectra were obtained on a Spectronic 3000 diode array spectrophotometer. ^1H NMR spectra were performed on a Bruker AC-250 P instrument with CD_2Cl_2 as solvent. All peak positions are relative to TMS. The experimental conditions for the COSY were as follows: 128 FIDs of eight scans each, data size 1 K, were collected. After digital filtering (sine bell window function), the FID was zero filled to 512 W in the F_1 dimension. Acquisition parameters were SW1 = 249.004 Hz, SW2 = 498.008 Hz for $[ReCl(CO)_3(tpt)]$ and SW1 = 191.865 Hz, SW2 = 383.730 Hz for $[(CO)_3ClRe(tpt)Zn(hfac)_2]$; recycle time 1.0 s. Magnetic susceptibilities at room temperature were measured by the Faraday method using a Cahn RM-2 balance. Cyclic voltammograms were obtained in MeCN containing 0.10 M $TBAPF_6$ as supporting electrolyte. The three electrode measurements were carried out with a Wenking Potentioscan POS-73 and an *X–Y* recorder. A platinum-disc working electrode, a platinum wire auxiliary electrode and an AgCl/Ag reference electrode (with internal reference ferrocenium/ferrocene) were used in the cyclic voltammetry experiments.

Synthesis of $[ReCl(CO)_3(dppt)]$ *and* $[ReCl(CO)_3(tpt)]$

An example of the general procedure is the following. $[ReCl(CO)_3(tpt)]$: a methanol (10 cm^3) solution of $[ReCl(CO)_5]$ (0.120 g, 0.332 mmol) and tpt (0.104 g, 0.332 mmol) was refluxed under nitrogen for 4 h. On cooling, red crystals precipitated which were collected by filtration, washed with methanol (3 × 4 cm^3) and dried *in vacuo* (0.090 g, 44% yield). With the dppt ligand, red needle-like crystals of $[ReCl(CO)_3(dppt)]$ (78% yield) were obtained. The results of the elemental analysis are presented in Table 1.

Synthesis of $[(CO)_3ClRe(tpt)M(hfac)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn)

All these complexes were isolated by reaction of $[ReCl(CO)_3(tpt)]$ with $[M(hfac)_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn) in CH_2Cl_2. The preparation below is typical.

$[(CO)_3ClRe(tpt)Zn(hfac)_2]\cdot 1/3C_6H_6$. A solution of $[ReCl(CO)_3(tpt)]$ (0.061 g, 0.099 mmol) and $[Zn(hfac)_2]\cdot 2H_2O$ (0.051 g, 0.099 mmol) in CH_2Cl_2 (15 cm^3) was stirred for 5 h. The deep red solution was then filtered, benzene (10 cm^3) was added to this solution and the total volume was then reduced *in vacuo* to *ca* 7–8 cm^3. From this solution a red–orange precipitate was obtained upon standing for 5 h. The solid was filtered and washed with benzene (2 × 3 cm^3) to give 0.085 g (76% yield) of the product in the form of red–orange needle-like crystals. The results of the elemental analyses of this zinc product and those for the crystalline manganese (orange, 84% yield), iron (dark brown, 57% yield), cobalt (orange, 90% yield), nickel (red, 65% yield) and copper (orange, 60% yield) analogues are presented in Table 1.

RESULTS AND DISCUSSION

Mononuclear complexes

Refluxing mixtures of $[ReCl(CO)_5]$ and L (L = dppt, tpt) in methanol in the molar ratio 1 : 1 afforded orange solutions, from which the red $[ReCl(CO)_3(L)]$ products were precipitated. These mononuclear complexes are air stable and soluble in organic solvents such as dichloromethane, acetone and benzene, slightly soluble in methanol and insoluble in light petroleum. The new rhenium(I) complexes $[ReCl(CO)_3(L)]$ have the *facial* structure

Table 1. Analytical data, IR spectra, visible spectra and magnetic moments for the complexes [ReCl(CO)$_3$(L)] (L = dppt, tpt) and [(CO)$_3$ClRe(tpt)M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn)

Compound	Analysis (%)[a]			IR (cm^{-1})[b]		μ_{eff}
	C	H	N	ν(CO)	$\lambda_{max}(\varepsilon)$[c]	(μ_B)
[ReCl(CO)$_3$(dppt)]	44.5 (44.8)	2.5 (2.3)	8.8 (9.1)	2023, 1945, 1900	435 (7490)	—
[ReCl(CO)$_3$(tpt)]	41.1 (40.8)	2.2 (2.0)	13.3 (13.6)	2023, 1928, 1908	445 (6790)	—
[(CO)$_3$ClRe(tpt)Mn(hfac)$_2$]	34.7 (34.3)	1.4 (1.3)	7.6 (7.7)	2029, 1932, 1916	468 (7100)	6.0
[(CO)$_3$ClRe(tpt)Fe(hfac)$_2$]	34.6 (34.2)	1.6 (1.3)	7.5 (7.7)	2031, 1930, 1917	469 (7650)	5.3
[(CO)$_3$ClRe(tpt)Co(hfac)$_2$]	34.4 (34.1)	1.5 (1.3)	7.5 (7.7)	2029, 1928, 1917	468 (7030)	4.8
[(CO)$_3$ClRe(tpt)Ni(hfac)$_2$]	35.2 (34.9)	1.4 (1.3)	7.6 (7.6)	2024, 1944, 1897	470 (7170)	3.2
[(CO)$_3$ClRe(tpt)Cu(hfac)$_2$]	35.0 (34.7)	1.5 (1.3)	7.5 (7.6)	2030, 1934, 1898	467 (7000)	1.9
[(CO)$_3$ClRe(tpt)Zn(hfac)$_2$] ·1/3C$_6$H$_6$	35.7 (36.0)	1.5 (1.4)	7.3 (7.4)	2023, 1933, 1905	470 (7150)	—

[a] Required values are given in parentheses.
[b] KBr discs, all bands are strong.
[c] In CH$_2$Cl$_2$ solution. λ_{max} in nm, ε values in M^{-1} cm^{-1}.

of the carbonyl groups. That is, their IR spectra show two strong carbonyl stretching bands (Table 1). The lower frequency band is split into two. The occurrence of a similar pattern has been observed in the related tricarbonyl complex *fac*-[ReCl(CO)$_3$(bpy)].[6]

The ^{1}H NMR spectra of the [ReCl(CO)$_3$(L)] complexes in CD$_2$Cl$_2$ are presented in Table 2, together with the previously assigned[1] signals of the uncomplexed ligands L (the atom labelling scheme is shown in Fig. 1). The assignments of the resonances of the [ReCl(CO)$_3$(L)] complexes were carried out by using 2D-COSY ^{1}H–^{1}H NMR spectroscopy and by comparison with the spectra of the free ligands. As an example, the COSY spectrum of the tpt compound [ReCl(CO)$_3$(tpt)] is displayed in Fig. 2. In this spectrum, the A ring protons appear as a separate set of four associate resonances, i.e. the two low-field doublets at 9.08 [H(6)] and 8.81 [H(3)] ppm are coupled with the triplet at 7.77 [H(5)] ppm and the multiplet at 8.22 [H(4)] ppm. These resonances are clearly displaced downfield with respect to the uncoordinated ligand tpt. The protons of the rings B and C appear in the remaining part of the spectrum as two superimposed sets of four associate resonances. By contrast with those of the A ring, the signals of the rings B and C are not shifted significantly from those of the uncomplexed ligand tpt. Consequently, the chelate action of tpt must occur through the nitrogen atoms of the pyridyl ring A and either the N(2) or N(4) atoms of the triazine ring. In the Fe^{II},[5]

Table 2. ^{1}H NMR chemical shifts,[a] in CD$_2$Cl$_2$, of the ligands L (dppt, tpt) and the complexes [ReCl(CO)$_3$(L)] and [(CO)$_3$ClRe(tpt)Zn(hfac)$_2$]

	Chemical shift							
Compound	H(6)	H(5)	H(4)	H(3)	H(6′), H(6″)	H(5′), H(5″)	H(4′), H(4″)	H(3′), H(3″)
dppt[b,c]	8.87dd	7.47m	7.92td	8.65dd				
tpt[b]	8.87dd	7.49m	7.94m	8.67dd	8.33dd (2H)	7.31m (2H)	7.89m (2H)	8.16m (2H)
[ReCl(CO)$_3$(dppt)][d]	9.06dd	7.73m	8.21td	8.78dd				
[ReCl(CO)$_3$(tpt)]	9.08dd	7.77td	8.22m	8.81dd	8.36m (2H)	7.42m (2H)	7.97m (2H)	8.26m (2H)
[(CO)$_3$ClRe(tpt)	9.12dd	7.81m	8.25td	8.75d	8.92d (1H)	7.78m (1H)	8.16m (1H)	8.21m (1H)
Zn(hfac)$_2$][e]					8.77d (1H)	7.75m (1H)	8.05d (1H)	8.18m (1H)

[a] Shifts are in ppm from TMS.
[b] Reference 1.
[c] Phenyl protons (10H): 7.70–7.32 ppm (from ref. 1).
[d] Phenyl protons (10H): 7.76–7.40 ppm.
[e] The protons of the hfac anion (2H) appear at 5.95 ppm as a singlet.

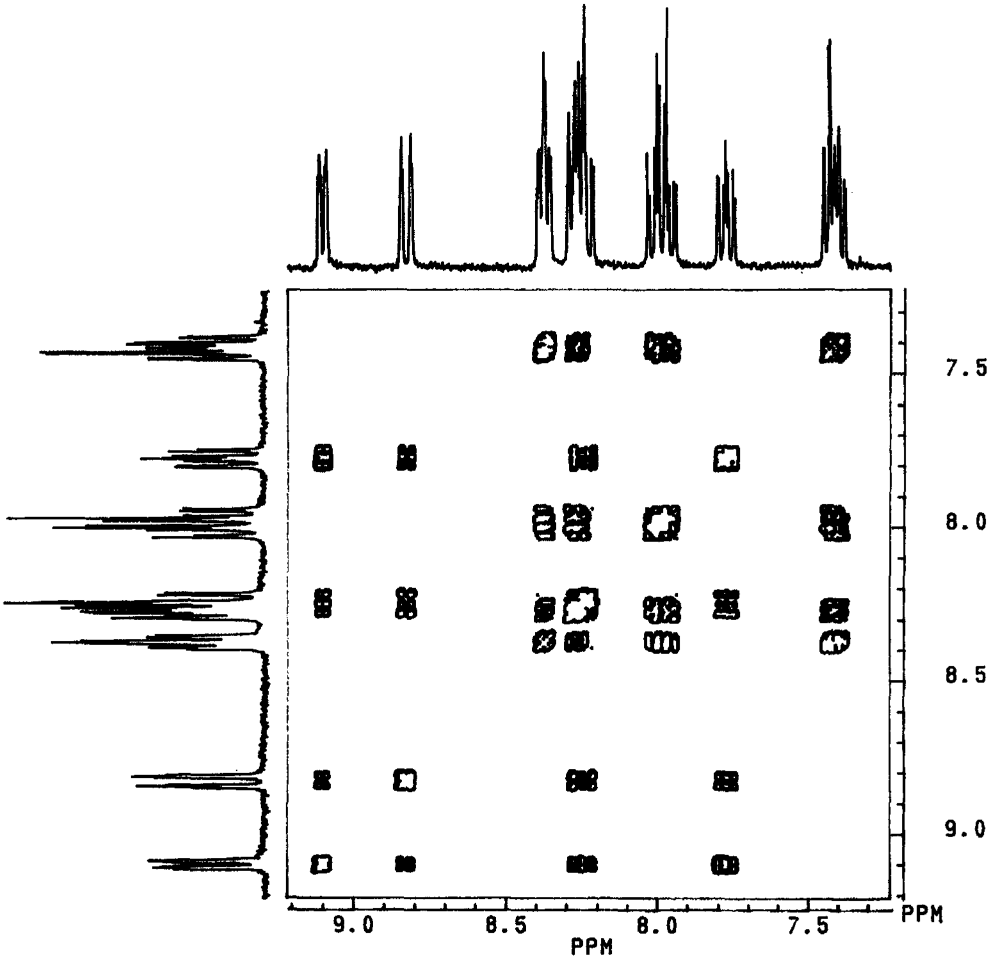


Fig. 2. 2D COSY spectrum of [ReCl(CO)$_3$(tpt)] in CD$_2$Cl$_2$.

Ru^{II}[7] and Mo^{0}[1] complexes with tpt, it was suggested that the triazine ligand is bonded through the N(2) atom, because in this situation the degree of steric hindrance between the non-bonded pyridyl groups and the other ligands next to them is the smallest. Likewise, the ^{1}H NMR spectroscopic features of the [ReCl(CO)$_3$(dppt)] complex (downfield shift of the pyridyl ring upon coordination) also suggest that the Re—dppt bonding involves the pyridyl N(1) and the triazine N(2) nitrogen atoms of the dppt ligand.

The electronic spectra in the visible region of the complexes [ReCl(CO)$_3$(L)] are characterized by a broad solvatochromic absorption in the range 350–550 nm (Table 1). Similar absorptions have been observed in tricarbonyl–rhenium(I) complexes containing polypyridyl ligands[8–10] and have been assigned to a metal-to-ligand charge transfer (MLCT) transition L(π^*) ← Re($d\pi$). The negative solvatochromism,[11] i.e. blue shift of the MLCT transition when the solvent polarity increases, of the [ReCl(CO)$_3$(L)] complexes was evaluated by plotting the MLCT absorption energies ($\bar{\nu}_{\mathrm{MLCT}}$, cm^{-1}) vs the E^*_{MLCT} parameter[12] (Table 3). The straight lines obtained are described by the equation $\bar{\nu}_{\mathrm{MLCT}} = A + B \cdot E^*_{\mathrm{MLCT}}$ (dppt: $A = 20{,}720$, $B = 3687$ cm^{-1}, $r = 0.983$; tpt: $A = 20{,}473$, $B = 3097$ cm^{-1}, $r = 0.983$). The difference in slope B, i.e. the solvent sensitivity, between the [ReCl(CO)$_3$(L)] complexes (dppt > tpt) can be explained in a similar way to that for the [Mo(CO)$_4$(L)] complexes.[1] That is, an enhancing of the negative solvatochromism should be expected by increasing the charge transfer character of the MLCT transition L(π^*) → Re($d\pi$) of the [ReCl(CO)$_3$(L)] compounds; in other words, by increasing the gap between the π^* orbital (LUMO) and the $d\pi$ orbital (HOMO) of the MLCT transition. Then, according to the electronic spectra (Table 1) the negative solvatochromism in the [ReCl(CO)$_3$(dppt)] complex is higher than that of [ReCl(CO)$_3$(tpt)]; the MLCT dppt(π^*) → Re($d\pi$) transition of the [ReCl(CO)$_3$(dppt)] complex is blue shifted by 10 nm with respect to that of

Table 3. Low-energy visible absorption maxima (cm^{-1}) of the complexes [ReCl(CO)$_3$(dppt)] and [ReCl(CO)$_3$(tpt)] in several solvents

Solvent (E^*_{MLCT})[a]	[ReCl(CO)$_3$(dppt)]	[ReCl(CO)$_3$(tpt)]
CCl$_4$ (0.12)	21,010	20,700
Benzene (0.34)	21,930	21,410
CHCl$_3$ (0.42)	22,730	22,170
THF (0.59)	22,780	22,270
CH$_2$Cl$_2$ (0.67)	22,990	22,470
Acetone (0.82)	23,810	23,040
MeCN (0.98)	24,210	23,370
DMSO (1.00)	24,510	23,640

[a] Solvent parameters (E^*_{MLCT}) from ref. 12.

[ReCl(CO)$_3$(tpt)]. The CV data make the nature of this blue shift clear. The one-electron oxidations of the [ReCl(CO)$_3$(L)] complexes do not differ greatly and occur as an irreversible wave (around 1.02 V) of the metal centre ($+1/+2$). On the opposite side, the ligand-centred first reduction waves are reversible but the $E_{1/2}$ value of the [ReCl(CO)$_3$(dppt)] complex (-1.30 V) is more negative than that observed for [ReCl(CO)$_3$(tpt)] (-1.17 V). Therefore, the results show that the LUMO of the [ReCl(CO)$_3$(dppt)] complex is shifted to higher energy with respect to that of the tpt complex [ReCl(CO)$_3$(tpt)], evidencing the decreased electron withdrawing action of the phenyl groups of the dppt ligand compared to the uncoordinated pyridyl groups of the tpt ligand.

Heterobinuclear complexes

The mononuclear tpt complex [ReCl(CO)$_3$(tpt)] reacts at room temperature in dichloromethane solution with [M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn) to afford the heterobinuclear products [(CO)$_3$ClRe(tpt)M(hfac)$_2$]. The related tricarbonyl complex [ReCl(CO)$_3$(dppt)] does not present this kind of reaction. The new bimetallic complexes [(CO)$_3$ClRe(tpt)M(hfac)$_2$] are soluble in CH$_2$Cl$_2$, slightly soluble in benzene, but undergo dissociation in polar solvents such as acetone to give the initial components [ReCl(CO)$_3$(tpt)] and [M(hfac)$_2$], as evidenced by the electronic spectra. The IR spectra of the Re—tpt—M complexes are clearly consistent with the retention of the *facial* carbonyl structure shown by the parent [ReCl(CO)$_3$(tpt)] complex (Table 1).

Figure 3 shows the 2D-COSY ^{1}H–^{1}H NMR spectrum of the complex [(CO)$_3$ClRe(tpt)Zn(hfac)$_2$] in CD$_2$Cl$_2$ and the assignments of the signals are given in Table 2. The pyridyl resonances (rings A, B and C) are detected as three different sets of protons, each one containing four protons. The resonances of the doublet furthest downfield at 9.12 [H(6)] ppm and its connected protons at 7.81 [H(5)], 8.25 [H(4)] and 8.75 [H(3)] ppm are assigned to ring A, since they occur close to the chemical shift of those of the metalloligand [ReCl(CO)$_3$(tpt)]. So, the other two sets of protons must belong to rings B and C. The resonances of these last sets of protons present a different behaviour in comparison with those of ring A. In particular, the protons nearest to the nitrogen atoms of rings B and C suffer a clear downfield shift on going from the mononuclear Re—tpt system to the bimetallic Re—tpt—M array [H(6′), H(6″): 0.56 and 0.41 ppm; H(5′), H(5″): 0.36 and 0.33 ppm]. Consequently, these results seem to be in accordance with a bidentate coordination of the metalloligand [ReCl(CO)$_3$(tpt)], involving only the nitrogen atoms of its free pyridyl groups (Fig. 4).

The absorption maxima data, in CH$_2$Cl$_2$, of the MLCT transition tpt(π^*) $\leftarrow$ Re($d\pi$) of the complexes [(CO)$_3$ClRe(tpt)M(hfac)$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn) are listed in Table 1. Since the position and behaviour of all these bands are quite similar, it seems reasonable to suggest that the bis-pyridyl nitrogen chelating action exhibited for the tpt ligand in the [(CO)$_3$ClRe(tpt)Zn(hfac)$_2$] complex is also present in the other members of the series of Re—tpt—M compounds. Also, the MLCT transition tpt(π^*) $\leftarrow$ Re($d\pi$) of the monomer [ReCl(CO)$_3$(tpt)] complex is red-shifted upon addition of the second metal centre to give the [(CO)$_3$ClRe(tpt)M(hfac)$_2$] complexes (Table 1). This kind of shift has been observed by several other authors in complexes containing the closely related bis-chelating polypyridyl ligands 2,3-bis(2-pyridyl)pyrazine,[8–10] 2,3-bis(2-pyridyl)quinoxaline[8,9] and 2,3-bis(2-pyridyl)benzo[g]quinoxaline.[8] It has been argued[8] that the decrease in energy of the mononuclear vs binuclear MLCT

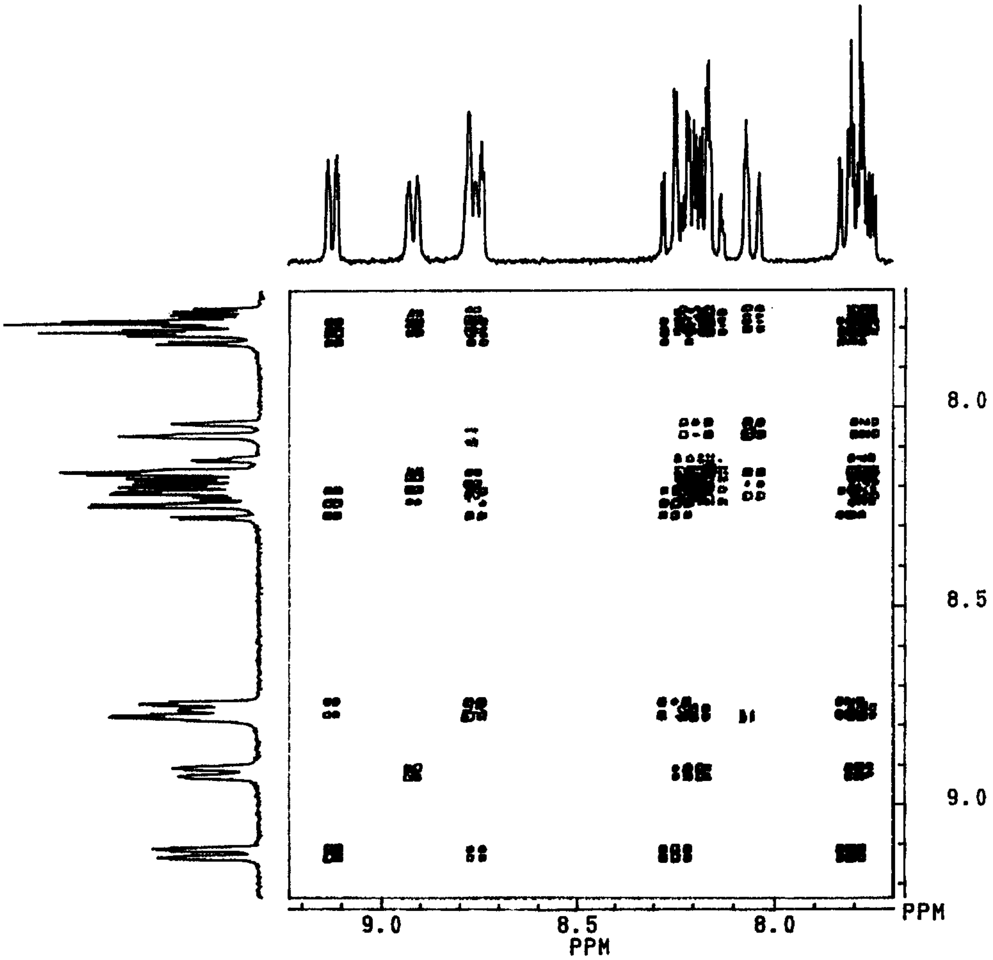


Fig. 3. 2D COSY spectrum of [$(CO)_3ClRe(tpt)Zn(hfac)_2$] in CD_2Cl_2.

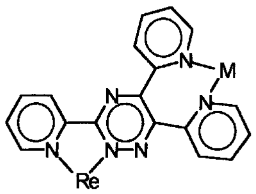


Fig. 4. Representation of the proposed coordination mode of the bridging ligand tpt.

transition is attributable to a stabilization of the π^* orbital of the bridging ligand by way of its interaction with the acidic second metal fragment.

Finally, the magnetic moments (Table 1) of the paramagnetic mixed-metal complexes [$(CO)_3ClRe(tpt)M(hfac)_2$] (M = Mn, Fe, Co, Ni, Cu) are consistent with M^{II} in an octahedral environment, and with Mn^{II}, Fe^{II} and Co^{II} in high-spin.[13] In spite of that, the *d–d* bands of the M^{II} species in the visible region were not observed due to the overlap of the most intense MLTC tpt(π^*) ← Re($d\pi$) transitions.

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