Inorganica Chimica Acta, *143* (1988) 89–93

Group VI Metal Tetracarbonyl Complexes with 3,6-Bis(2′-pyridyl)pyridazine and 7,10-Bis(2′-pyridyl)-8,9-diazafluoranthene

MAURO GHEDINI*, FRANCESCO NEVE and MARIA CLOTILDE BRUNO

Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

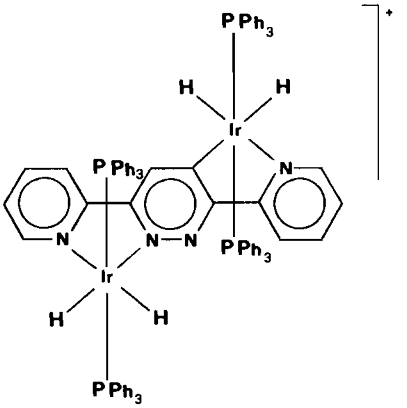
(Received May 22, 1987)

Abstract

In a comparative study, group VI tetracarbonyl complexes with 3,6-bis(2′-pyridyl)pyridazine (dppn) and 7,10-bis(2′-pyridyl)-8,9-diazafluoranthene (dpaf) have been synthesized and characterized by elemental analyses, IR, ^{1}H NMR and electronic spectroscopy. The energy of the first MLCT electronic transition, for each ligand follows the order Mo > W > Cr, and shows that dpaf undergoes the stronger back-bonding interaction. Hitherto, no other examples of 7,10-bis(2′-pyridyl)-8,9-diazafluoranthene transition metal complexes have been reported.

Introduction

In recent studies we have investigated the ability of 3,6-bis(2′-pyridyl)pyridazine (dppn) as ligand in the preparation of mono and binuclear group VIII transition metal complexes. In this field we reported the syntheses of mononuclear Ir(I) carbonyl or nitrosyl complexes [1] and a series of side-by-side heteronuclear bimetallic compounds [2–4]. Moreover, exploring the chemistry of iridium dihydrido species, we synthesized the *trans* bimetallic complex, reported in Scheme 1, featuring an unusual Ir–C(pyridazinic) bond [5].



Scheme 1. Sketch of the structure of the cation of the bimetallic iridium dppn hydrido complex.

In a further study on Pt(II) dimethyl or diphenyl dppn organometallic derivatives we characterized such a ligand with respect its σ-donor and π-acceptor ability and a comparison with other similar nitrogen containing chelate systems was done [6]. The results we obtained indicate that dppn is a strong stabilizing ligand on the basis of the energy of the first MLCT electronic transition. We report now the reactivity of this ligand toward group VI metal tetracarbonyl complexes.

Several compounds are known from the literature wherein the $M(CO)_4$ moiety ($M = Cr$, Mo, W) is coordinated to a mono or to a bis-chelating nitrogen containing molecule. To the former class of ligands belong 2,2′-bipyridine (bipy) [7, 8] and the coupled bidiazines 3,3′-bipyridazine (bpdz) [9], 4,4′-bipyrimidine (bpm) [9] and 2,2′-bipyrazine (bpz) [9, 10] examples of the latter class are 2,2′-bipyrimidine (bpym) [8, 9, 11], 2,5-bis(2′-pyridyl)pyrazine (bppz) [12], 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (bptz) [12], azo-2,2′-bipyridine (abpy) [12] and 2,3-bis(2′-pyridyl)pyrazine (dpp) [13]. Within this context it appeared interesting to extend the study also to the synthesis and characterization of $M(CO)_4$ 7,10-bis(2′-pyridyl)-8,9-diazafluoranthene, dpaf (Fig. 1), derivatives. Remarkably, to the best of our knowledge, these species are the first examples of dpaf transition metal complexes so far reported.

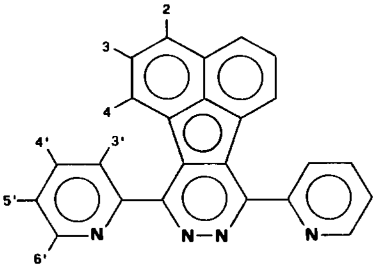


Fig. 1. 7,10-Bis-(2′-pyridyl)-8,9-diazafluoranthene.

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

Experimental

All organometallic compounds were synthesized under an inert atmosphere with use of dried solvents.

^{1}H NMR spectra were run on a Bruker WH 300 spectrometer with TMS as internal standard. Infrared spectra were recorded from THF solutions on a Perkin-Elmer 1330 spectrometer. Electronic spectra were obtained using a Perkin-Elmer 550 SE spectrophotometer. Elemental analyses were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Italy.

The ligand 3,6-bis(2′-pyridyl)pyridazine was obtained according to Butte and Case [14]. 7,10-bis-(2′-pyridyl)-8,9-diazafluoranthene was synthesized according to the literature method [15] and characterized by ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.59 (ddd, $H_{5'}$), 7.69 (dd, H_3), 8.06 (vt, $H_{4'}$) 8.12 (dd, H_2), 8.30 (ddd, $H_{3'}$), 8.41 (dd, H_4), 8.94 (ddd, $H_{6'}$); $J_{2,3} = 8.2$, $J_{3,4} = 7.3$, $J_{2,4} = 0.5$, $J_{5',6'} = 4.9$, $J_{4',6'} = 1.8$, $J_{4',5} = 7.7$, $J_{3',4'} = 7.9$, $J_{3',5} = 1.0$, $J_{3',6'} = 1.0$ Hz.

The tetracarbonyl complexes (NBD)M(CO)$_4$ M = Cr, Mo, W; NBD = 2,5-norbornadiene) were synthesized by the standard method [16].

(dppn)Cr(CO)$_4$ (1)

A solution of 25 mg (0.098 mmol) of (NBD)Cr(CO)$_4$ in tetrahydrofuran (THF) (3 ml) was added to a stirred solution of 23 mg (0.098 mmol) of dppn in THF (2 ml). The resulting deep violet solution was allowed to stand for 12 h. Addition of diethyl ether/petroleum ether (2:1) (15 ml) gave a dark violet solid. The product was collected by filtration and vacuum dried; yield 30 mg (75%). *Anal.* Calc. for $C_{18}H_{10}CrN_4O_4$: C, 54.29; H, 2.53; N, 14.07. Found: C, 53.59; H, 2.85; N, 15.35%.

(dppn)Mo(CO)$_4$ (2)

A solution of 100 mg (0.33 mmol) of (NBD)Mo(CO)$_4$ in benzene (3 ml) was added to a solution of 78 mg (0.33 mmol) of dppn in benzene (7 ml). The solution turned deep red. After stirring for 12 h a microcrystalline brown solid, precipitated from the solution, was collected by filtration, washed with diethyl ether and vacuum dried; yield 100 mg (68%). *Anal.* Calc. for $C_{18}H_{10}MoN_4O_4$: C, 48.89; H, 2.28; N, 12.67. Found: C, 49.27; H, 2.13; N, 12.49%.

(dppn)W(CO)$_4$ (3)

dppn (150 mg, 0.64 mmol) and W(CO)$_6$ (225 mg, 0.64 mmol) were heated under reflux in xylene solution (30 ml) for 24 h. A dark violet microcrystalline solid was obtained on cooling the reaction mixture. The product was filtered, washed with petroleum ether and vacuum dried; yield 225 mg (75%). *Anal.* Calc. for $C_{18}H_{10}N_4O_4W$: C, 40.78; H, 1.90; N, 10.57. Found: C, 41.53; H, 1.93; N, 10.73%.

(dpaf)Cr(CO)$_4$ (4)

To a suspension of 42 mg (0.117 mmol) of dpaf in THF (5 ml) were added 30 mg (0.117 mmol) of (NBD)Cr(CO)$_4$. The resulting green mixture was stirred for 12 h. After this time the dark violet solid formed was collected by filtration, washed with diethyl ether and vacuum dried; yield 51 mg (82%). *Anal.* Calc. for $C_{28}H_{14}CrN_4O_4$: C, 64.37; H, 2.70; N, 10.72. Found: C, 63.19; H, 2.69; N, 10.47%.

(dpaf)Mo(CO)$_4$ (5)

A solution of 100 mg (0.33 mmol) of (NBD)Mo(CO)$_4$ in benzene (4 ml) was added to a suspension of 119 mg (0.33 mmol) of dpaf in benzene (6 ml) and the reaction mixture stirred for 14 h. After this time a dark brown solid was formed which was collected by filtration, washed with diethyl ether and vacuum dried; yield 140 mg (74%). *Anal.* Calc. for $C_{28}H_{14}MoN_4O_4$: C, 59.38; H, 2.49; N, 9.89. Found: C, 58.71; H, 2.38; N, 9.44%.

(dpaf)W(CO)$_4$ (6)

The dpat derivative was obtained by the same procedure described for **3** with a reaction time of 24 h. Yield 85%. *Anal.* Calc. for $C_{28}H_{14}N_4O_4W$: C, 51.40; H, 2.16; N, 8.56. Found: C, 52.09; H, 2.51; N, 8.31%.

Results and Discussion

The tetracarbonyl dppn or dpaf group VI metal complexes (**1**–**6** in Table I) were synthesized by reacting the appropriate chelate ligand with (NBD)M(CO)$_4$ (M = Cr, Mo) or with W(CO)$_6$. The (dppn)M(CO)$_4$ derivatives (**1**, M = Cr; **2**, M = Mo) as well as their dpaf analogues **4** (M = Cr) and **5** (M = Mo), were obtained in good yield (*ca.* 75%) in mild conditions (room temperature, THF or benzene solutions, respectively), while the tungsten complexes **3** and **6** can be prepared in refluxing xylene starting from W(CO)$_6$ (yield%: **4**, 75; **6**, 85). The compounds so formed were characterized by elemental analysis ('Experimental'), which accounts for the expected hexacoordinated species, and IR, ^{1}H NMR and electronic spectroscopy.

The IR spectra of **1**–**6** were run either as solid samples (KBr pellets) or in THF solutions. In the carbonyl stretching region, while as solids they display three not well resolved absorptions, in solution four distinct bands, according to the literature data for similar octahedral tetracarbonyl compounds [12], are observed (Table I). Moreover, with regard to the chelating ligand, both dppn and dpaf show

TABLE I. CO Stretching Frequencies ν(CO) (cm^{-1}) of Complexes 1–6[a]

Complex		ν(CO)			
1	(dppn)Cr(CO)$_4$	1985(m)	1936(br,m)	1877(vs)	1827(s)
2	(dppn)Mo(CO)$_4$	1989(m)	1930(br,m)	1876(vs)	1828(s)
3	(dppn)W(CO)$_4$	1981(m)	1939(br,m)	1866(vs)	1823(s)
4	(dpaf)Cr(CO)$_4$	1982(m)	1941(br,m)	1873(vs)	1823(s)
5	(dpaf)Mo(CO)$_4$	1990(m)	1944(br,m)	1875(vs)	1821(s)
6	(dpaf)W(CO)$_4$	1982(m)	1939(br,m)	1864(vs)	1820(s)

[a] In THF solution.

TABLE II. ^{1}H NMR Data (δ)[a] of (dppn)M(CO)$_4$ Complexes (M = Cr, Mo, W)

Compound	H_6	H_5	H_4	H_3	$H_{6'}$	$H_{5'}$	$H_{4'}$	$H_{3'}$	H_4(pz)	H_5(pz)
dppn[b]	8.73	7.43	7.93	8.72					8.67	
(dppn)Cr(CO)$_4$[c]	9.31	7.48	7.98	8.12	8.75	7.43	7.93	8.84	8.73	8.22
(dppn)Mo(CO)$_4$[d]	9.23	7.51	8.04	8.21	8.76	7.50	7.99	8.78	8.82	8.34
(dppn)W(CO)$_4$[e]	9.35	7.52	8.06	8.25	8.77	7.51	8.01	8.79	8.85	8.38

[a] From 300 MHz spectra in CD_2Cl_2 solutions at 20 °C. Chemical shifts are relative to Me_4Si. [b] Ref. 1. [c] $J_{5,6} = 5.1; J_{3,4} = 8.3; J_{3',4'} = 8.6; J_{4,5}(pz) = 9.0$ Hz. [d] $J_{5,6} = 5.4; J_{4,5} = 7.6; J_{3,4} = 8.1; J_{4,6} = 1.7; J_{3,5} = 1.2; J_{3,6} = 0.9; J_{5',6'} = 4.7; J_{4',5'} = 7.8; J_{4',6'} = 1.8; J_{3',4'} = 8.1; J_{3',5'} = 1.3; J_{3',6'} = 0.9; J_{4,5}(pz) = 9.1$ Hz. [e] $J_{4,5} = 7.6; J_{4,6} = 1.5; J_{3,4} = 8.2; J_{3,5} = 1.2; J_{5',6'} = 5.0; J_{4',5'} = 7.6; J_{4',6'} = 1.8; J_{3',4'} = 7.8; J_{3',5'} = 1.2; J_{4,5}(pz) = 9.0$ Hz.

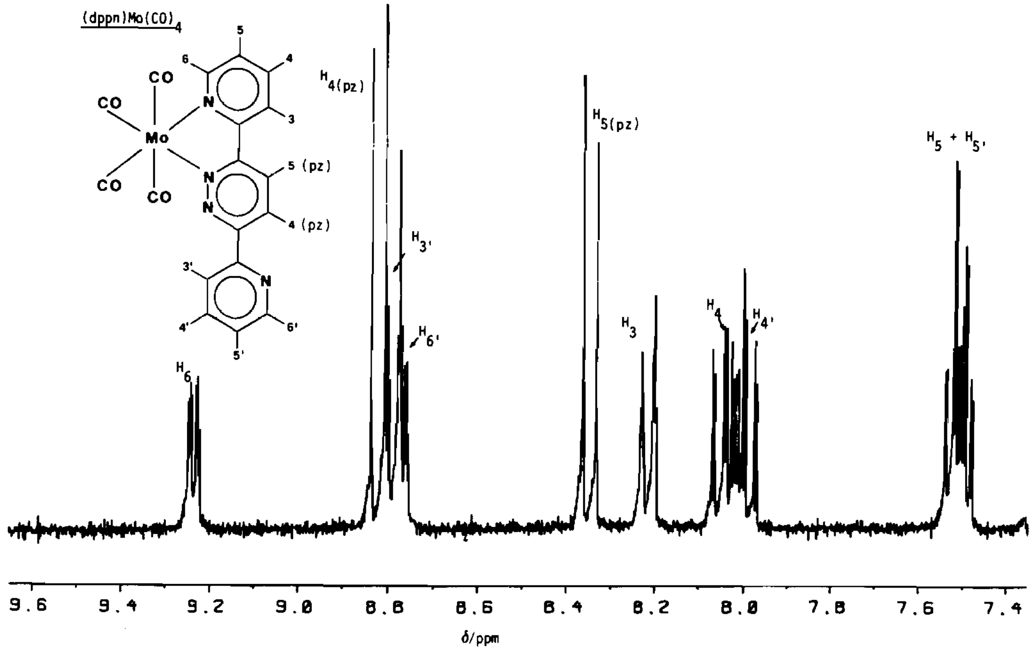


Fig. 2. ^{1}H NMR spectrum (300 MHz) at 20 °C of (dppn)Mo(CO)$_4$ (2) in the range 7.4–9.6 ppm.

the spectral pattern, previously discussed for dppn [4], characteristic for a mono-metallic complexation.

Further evidences about the dppn coordination mode arise from the ^{1}H NMR spectra, as shown in Fig. 2 for (dppn)Mo(CO)$_4$ (2). The spectral multiplicity of 1–3 displays two sets of pyridyl protons (Table II), attributable to the coordinated and uncoordinated moieties [1]. Typically, in the former set, the shifts upon coordination follow the order $H_6 > H_3 > H_4 > H_5$.

For the pyridazine protons, two distinct signals are observed. They are downfield and upfield shifted with respect to uncomplexed dppn and therefore are assigned to H_4(pz) and to H_5(pz) respectively [1].

Worthy of note is the position of the H_3 and H_5(pz) signals: they both are found shifted upfield, as for the (bipy)Mo(CO)$_4$ complex [8], and in contrast to what is known for other LM(CO)$_4$ species (M = Cr, Mo, W; L = bpdz, bpm [9] or bpz [9, 10]), where protons in the *meta*-position with respect to the nitrogen atoms involved in the metal coordination are found downfield shifted. This deshielding was explained by Crutchley and Lever [10] in terms of van der Waals interaction between the two H_3 protons which should be forced together by the *cis* conformation assumed by the chelating ligand upon coordination. Nevertheless, when L is either dppn or bipy the homologous protons, although in a similar geometrical environment, are shielded. Therefore the chemical shift of these protons seems to depend on two opposite effects, of which the shielding one is dominating in dppn and bipy complexes.

With regard to the dpaf derivatives **4–6**, either the dissociative instability (particularly for the Cr complex, **4**) or the poor solubility in the usual organic solvents, prevented any NMR investigation.

The electronic spectra of both dppn and dpaf tetracarbonyl complexes have been recorded in three different solvents, namely toluene, THF and acetone, which in the solvent polarity scale defined by Manuta and Lees [17] have E^*_{MLCT} values ranging from 0.30 (toluene) to 0.82 (acetone). The band in the lowest energy region of the spectra, λ_1 ($\epsilon > 10^3 \times 1$ M^{-1} cm^{-1}, Table III) displays the characteristic negative solvatochromism and was assigned to MLCT ($\pi^* \leftarrow d$) transition [18].

In all the considered solvents and for each metal, λ_1(dppn) > λ_1(dpaf). Since the lowering of the λ_1 value is evidence of an increased back-bonding interaction between the M(CO)$_4$ moiety and the nitrogen containing ligand [9], it can be concluded that dpaf undergoes a stronger interaction than dppn does. So that, integrating these results within the literature data concerning other similar ligands [8, 13] involved in LM(CO)$_4$ complexes, the back-bonding interaction ability scale became as follows: bptz > abpy ⩾ bpm > bpdz > dpaf > bpz > dppn > bpym > bipy.

On the other hand, according with the reported trend [17, 18], for the different metals, both in dppn and dpaf complexes, in any particular solvent, the order of λ_1 values (Table III) is Mo > W > Cr.

Finally, some considerations can be made for dpaf as a ligand. This species was chosen because it is strictly similar to dppn as regards the coordination behaviour but, in addition, since reactions on the pyridazine ring (e.g. metallation [5]) are prevented, it can act uniquely as a *cis*-dinucleating bis-chelate ligand. The reaction conditions in which dpaf complexes **4–6** are formed are similar to those used for the dppn homologues (**1–3**) and they are generally less soluble than **1–3**. Moreover, the stronger back-bonding interaction undergone by dpaf with respect to dppn can be related to the presence of the fused acenaphto system.

Keeping these results in mind and the attention that has recently been focused on similar ligands [12, 13, 19], the coordination chemistry of 7,10-bis-(2′-pyridyl)-8,9-diazafluoranthene appears to be worthy of further extensive investigations.

Acknowledgements

This work has been supported by the Italian Ministero della Pubblica Istruzione. We also thank Professor G. Denti for helpful discussions.

References

1 M. Ghedini, M. Longeri and F. Neve, *J. Chem. Soc., Dalton Trans.*, 2669 (1986).

2 A. Tiripicchio, A. M. Manotti Lanfredi, M. Ghedini and F. Neve, *J. Chem. Soc., Chem. Commun.*, 97 (1983).

TABLE III. Low Energy MLCT Absorption Maxima λ (cm^{-1})[a] of the Complexes (L)M(CO)$_4$ (M = Cr, Mo, W; L = dppn, dpaf)[b]

Complex	λ		
	Toluene (0.30)[b]	THF (0.59)[b]	Acetone (0.82)[b]
1 (dppn)Cr(CO)$_4$	17301	18622(3.17)	19157
2 (dppn)Mo(CO)$_4$	18116	19268(3.79)	20202
3 (dppn)W(CO)$_4$	17544	18726(3.90)	19493
4 (dpaf)Cr(CO)$_4$	16207	16722(3.60)	17422
5 (dpaf)Mo(CO)$_4$	17482	18349(3.92)	19048
6 (dpaf)W(CO)$_4$	17241	17825(3.76)	18622

[a] Log ε (ε in l mol^{-1} cm^{-1}) given in parentheses. [b] Solvent parameters (in parentheses) from ref. 17.

3 M. Ghedini and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1417 (1984).
4 M. Ghedini, F. Neve, F. Morazzoni and C. Oliva, *Polyhedron, 4,* 497 (1985).
5 M. Ghedini, A. M. Manotti Lanfredi, F. Neve, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, in press.
6 M. Ghedini, M. Longeri and F. Neve, *Inorg. Chim. Acta, 132,* 223 (1987).
7 M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).
8 C. Overton and J. A. Connor, *Polyhedron, 1,* 53 (1982).
9 S. Ernst and W. Kaim, *J. Am. Chem. Soc., 108,* 3578 (1986).
10 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem., 21,* 2276 (1982).
11 K. J. Moore and J. S. Petersen, *Polyhedron, 2,* 279 (1983).
12 W. Kaim and S. Kohlman, *Inorg. Chem., 26,* 68 (1987).
13 R. R. Ruminski and J. O. Johnson, *Inorg. Chem., 26,* 210 (1987).
14 W. Butte and F. H. Case, *J. Org. Chem., 26,* 4690 (1961).
15 T. Sasaki, K. Kanematsu and T. Hiramatsu, *J. Chem. Soc., Perkin Trans., 1,* 1213 (1974).
16 M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).
17 D. M. Manuta and A. J. Lees, *Inorg. Chem., 22,* 3825 (1983).
18 S. Ernst, Y. Kurth and W. Kaim, *J. Organomet. Chem., 302,* 211 (1986)
19 G. De Rosa, *Dr. Thesis*, Università della Calabria, 1984.