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FULL PAPER

Co-ordination properties of 1,10-phenanthroline-5,6-dione towards group 4 and 5 metals in low and high oxidation states†

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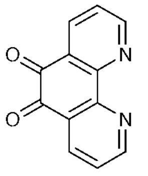
Received 26th July 1999, Accepted 28th October 1999

The molecular structure of 1,10-phenanthroline-5,6-dione has been determined by X-ray diffraction analysis. The compound reacts with the tetrachlorides of Group 4 metals affording adducts of general formula $[MCl_4(C_{12}H_6N_2O_2)]$ (M = Ti, Zr or Hf) and $[(MCl_4)_2(C_{12}H_6N_2O_2)]$ (M = Ti or Hf), *N,N′*- and *N,N′,O,O′*-co-ordinated respectively. The compound $[HfCl_4(C_{12}H_6N_2O_2)]$ is reactive towards $TiCl_4$ affording the bimetallic compound $[Cl_4Hf(C_{12}H_6N_2O_2)TiCl_4]$. The reaction of the dione with bis-cyclopentadienyl derivatives of titanium(II), zirconium(II), $[MCp_2(CO)_2]$, and vanadium(II), VCp_2, affords derivatives *O,O′*-co-ordinated to the MCp_2 moiety. By reaction of $[TiCp_2(C_{12}H_6N_2O_2)]$ with $[TiCp_2(CO)_2]$ the bimetallic derivative $[(TiCp_2)_2(C_{12}H_6N_2O_2)]$ is obtained, which is suggested to contain two $TiCp_2$ fragments, *O,O′*- and *N,N′*-co-ordinated to 1,10-phenanthroline-5,6-dione. The $[MCp_2(C_{12}H_6N_2O_2)]$ (M = Ti, Zr or V) derivatives react with $M'Cl_4$ (M′ = Ti or Hf) to give $[Cp_2M(C_{12}H_6N_2O_2)M'Cl_4]$ bimetallics.

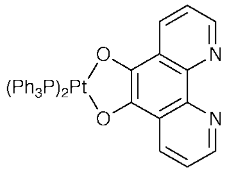
Introduction

Since the appearance of the Creutz–Taube cation and the discovery of its peculiar redox behaviour,[1] many efforts[2] have been made to synthesize bimetallic compounds containing unsaturated ligands such as functionalized quinones or polydentate heterocyclic amines which could establish electronic interactions between the metals centres.[3]

In the search for molecules characterized by extensive electronic delocalization and good co-ordinating properties, 1,10-phenanthroline-5,6-dione ($C_{12}H_6N_2O_2$), attracted our attention due to the presence of two co-ordinating functionalities in the same molecule (the quinonoid and the diimine). Moreover, the presence of two types of basic centres, nitrogen and oxygen atoms, both sp^2-hybridized, contributes to make this molecule an ideal system to study the different co-ordinating ability of the two sets of donor atoms.



Some years ago, Balch and co-workers[4] obtained $[Pt(PPh_3)_2(C_{12}H_6N_2O_2\text{-}O,O')]$ **1** and $[PdCl_2(C_{12}H_6N_2O_2\text{-}N,N')]$ **2** by reaction of the dione with platinum(0) or palladium(II) precursors, respectively, showing that the dione could interact with the metal centres through the quinonoid or the diiminic functionality. Moreover, Pierpont and co-workers[5] and Paw and Eisenberg[6] proved that it could behave as a bridging ligand with the synthesis of the structurally characterized bimetallic derivatives **3**–**5**.



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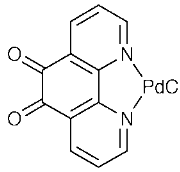

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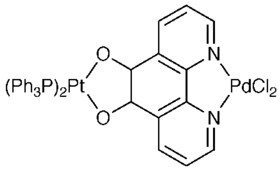

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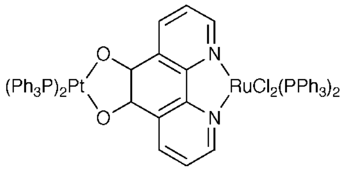

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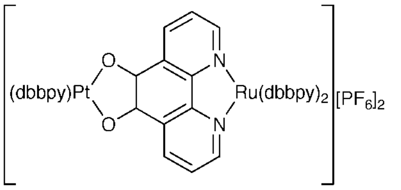

5 dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine

In the framework of our research program on the synthesis and the reactivity of co-ordination and organometallic compounds of early transition elements we decided to study the co-ordination and redox properties of the dione with respect to derivatives of Group 4 and 5 metals and this paper represents a contribution to this field.

Results and discussion

The study of the ligating properties of 1,10-phenanthroline-5,6-dione began with a reexamination of the synthetic procedure to this species. Although it has been known for about fifty years, and several synthetic procedures are reported,[7,8] we decided to

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4389/

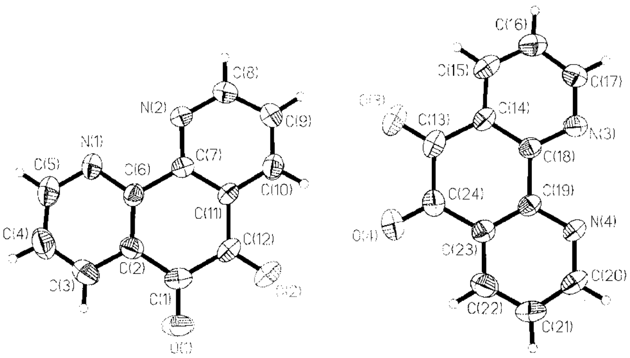
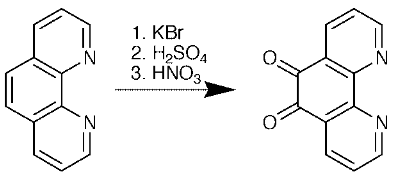


Fig. 1 View of the two independent molecules of 1,10-phenanthroline-5,6-dione, with the atom numbering scheme used.

follow the procedure reported by Yamada and co-workers[8] whereby 1,10-phenanthroline is oxidized by a mixture of concentrated sulfuric and nitric acids, see reaction sequence (1).



(1)

We have found that the critical point in this procedure is the treatment of the 1,10-phenanthroline/KBr mixture with sulfuric acid: it has to be performed by adding the heterocyclic diamine/KBr mixture to sulfuric acid pre-cooled at liquid nitrogen temperature (see Experimental section). Attempts to prepare the dione by mixing 1,10-phenanthroline, KBr and sulfuric acid at 0 °C, as reported by Yamada, afforded low yields (1–2%).

By slow evaporation of a solution of the dione in dichloromethane single crystals formed which were studied by X-ray diffraction methods. The asymmetric unit of 1,10-phenanthroline-5,6-dione consists of two independent molecules whose structure is shown in Fig. 1. The molecule is almost planar [maximum deviation 0.081 Å for O(1) in molecule 1 and 0.039 Å for N(3) in molecule 2] and placed on (2 1 $\bar{1}$) planes (interplanar distance = 3.628 Å). Table 1 lists a selection of bond distances and angles.

Owing to the fact that the compound is reminiscent of both 1,10-phenanthroline[9] and 9,10-phenanthrenequinone,[10] a metrical comparison of the three species is reported. In 1,10-phenanthroline the N–C bonds are the shortest (1.36 Å), while the C–C bonds joining the pyridyl rings are the longest (1.49 Å). Similarly, the dione shows the N–C bonds to be the shortest in both molecules (1.34 Å, mean values), with the exclusion of the C=O bonds, (1.210 Å average), to be compared with the mean value of 1.49 Å for the C(6)–C(7) and C(1)–C(18) bonds. At variance with 1,10-phenanthroline and similar to 9,10-phenanthrenequinone, the carbonyl groups make the distances C(1)–C(12) and C(13)–C(24) to be typical of single bonds (1.529 and 1.539 Å, respectively), to be compared with 1.570(8) Å in 9,10-phenanthrenequinone. Moreover, the CO bond distances are shorter (1.21 Å, mean value) than in 9,10-phenanthrenequinone [1.229(8) Å]: this, together with the higher stretching frequency of the C=O bond (1685 cm^{-1}, Nujol) with respect to 9,10-phenanthrenequinone (1675 cm^{-1}, Nujol), suggests that the carbonyl bond in the dione is stronger than in 9,10-phenanthrenequinone.

Fig. 2 shows a view of the packing of the $C_{12}H_6N_2O_2$ units. The lattice periodicity produces a stacking in the *a* direction: stacks of molecules of types 1 and 2 are built by the sequence of inversion centres spanned by *a*/2 and therefore subsequent molecules in each stack point their oxygen atoms in opposite directions. Owing to the inclination of the *a* axis with respect to the (2 1 $\bar{1}$) plane, the molecules of both stacks are tilted with respect to the stacking axes; moreover, the major axes of the molecules in stack A are almost perpendicular to those in stack B (Fig. 3).

Table 1 A selection of bond distances (Å) and angles (°) for 1,10-phenanthroline-5,6-dione. Numbers in parentheses are estimated standard deviations in the least significant digits

Molecule 1		Molecue 2	
O(1)–C(1)	1.213(3)	O(3)–C(13)	1.207(3)
C(1)–C(2)	1.477(4)	C(13)–C(14)	1.477(3)
C(1)–C(12)	1.529(4)	C(13)–C(24)	1.539(4)
C(5)–N(1)	1.335(3)	C(17)–N(3)	1.336(3)
N(1)–C(6)	1.343(3)	N(3)–C(18)	1.338(3)
C(6)–C(7)	1.489(3)	C(18)–C(19)	1.494(3)
C(7)–N(2)	1.339(3)	C(19)–N(4)	1.343(3)
N(2)–C(8)	1.339(3)	N(4)–C(20)	1.337(3)
C(12)–O(2)	1.208(3)	C(24)–O(4)	1.209(3)
O(1)–C(1)–C(2)	123.1(3)	O(3)–C(13)–C(14)	123.0(3)
O(1)–C(1)–C(12)	118.8(2)	O(3)–C(13)–C(24)	119.1(2)
C(2)–C(1)–C(12)	118.1(2)	C(14)–C(13)–C(24)	117.9(2)
N(1)–C(5)–C(4)	125.0(3)	N(3)–C(17)–C(16)	125.2(3)
C(5)–N(1)–C(6)	116.7(2)	C(17)–N(3)–C(18)	116.7(2)
N(1)–C(6)–C(2)	122.2(2)	N(3)–C(18)–C(14)	122.4(2)
N(1)–C(6)–C(7)	116.6(2)	N(3)–C(18)–C(19)	117.0(2)
N(2)–C(7)–C(11)	122.0(2)	N(4)–C(19)–C(23)	122.1(2)
N(2)–C(7)–C(6)	117.4(2)	N(4)–C(19)–C(18)	117.3(2)
N(2)–C(8)–C(9)	124.7(3)	N(4)–C(20)–C(21)	124.3(3)
C(7)–N(2)–C(8)	117.0(2)	C(20)–N(4)–C(19)	117.3(2)
O(2)–C(12)–C(1)	119.5(2)	O(4)–C(24)–C(13)	118.9(2)
O(2)–C(12)–C(11)	122.3(2)	O(4)–C(24)–C(23)	123.2(3)
C(11)–C(12)–C(1)	118.2(2)	C(23)–C(24)–C(13)	117.9(2)

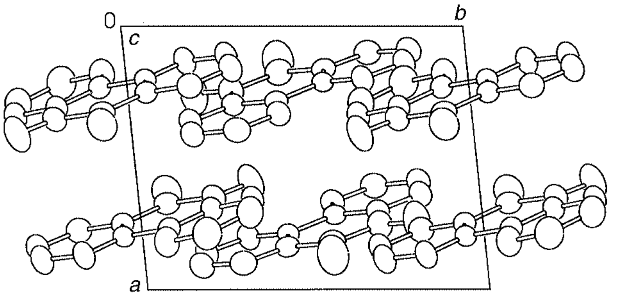
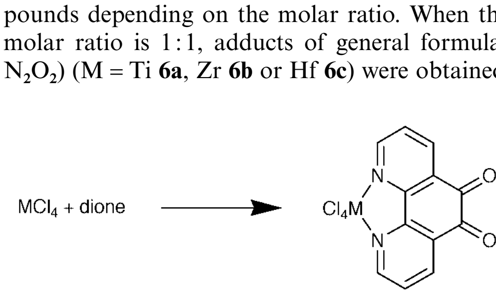


Fig. 2 View of the packing of the two crystallographically independent molecules of 1,10-phenanthroline-5,6-dione.

Reactivity of $C_{12}H_6N_2O_2$ with MCl_4 (M = Ti, Zr or Hf)

The reaction of the dione with MCl_4 affords two different compounds depending on the molar ratio. When the dione : MCl_4 molar ratio is 1 : 1, adducts of general formula $MCl_4(C_{12}H_6N_2O_2)$ (M = Ti **6a**, Zr **6b** or Hf **6c**) were obtained, eqn. (2). On the other hand, bimetallic compounds of formula $(MCl_4)_2(C_{12}H_6N_2O_2)$ (M = Ti **7a** or Zr **7b**), containing *O*,*O*′,*N*,*N*′-coordinated dione, were obtained when the molar ratio was 0.5 : 1, see reaction (3).



(2)

6a, M = Ti
6b, M = Zr
6c, M = Hf

The infrared spectra of compounds **6** and **7** are similar, the main differences being observed in the quinonoid stretching

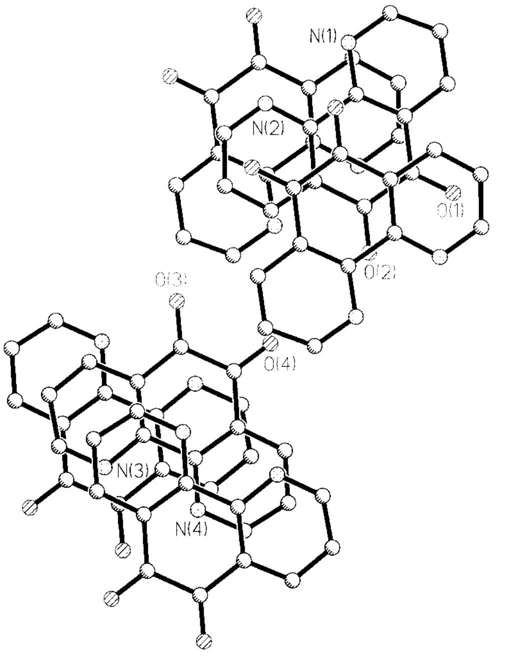
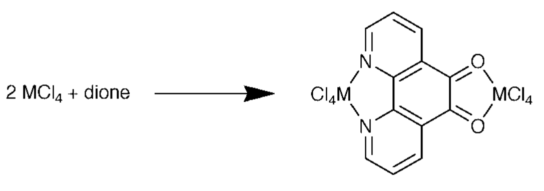


Fig. 3 View of the stacking (stacks A and B) of 1,10-phenanthroline-5,6-dione molecules.

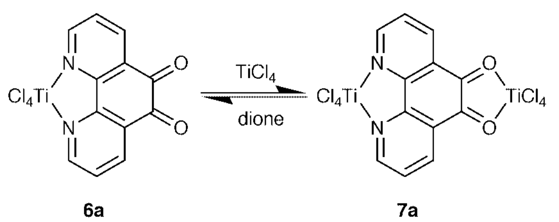


(3)

7a, M = Ti
7b, M = Zr

region. Strong absorptions are observed at about 1700 cm^{-1} for **6a–6c** and at about 1640 cm^{-1} for **7a**, **7b**. It is worth mentioning that $[PdCl_2(C_{12}H_6N_2O_2)]$[4] and $[Fe(C_{12}H_6N_2O_2)_3][PF_6]_2$,[11] formulated as *N*,*N*′-adducts of the dione, have absorptions at about 1700 cm^{-1} and that the $TiCl_4$ adduct of 9,10-phenanthrenequinone[12] shows the C=O stretching vibration at 1575 cm^{-1} (9,10-phenanthrenequinone absorbs at 1675 cm^{-1}, $\Delta\tilde{\nu}_{C=O} = -100$ cm^{-1}, Nujol mull). Therefore, by taking into consideration that the C=O stretching vibration of the dione is at 1685 cm^{-1} (Nujol mull), the higher wavenumber absorptions observed for **6a–6c** ($\Delta\tilde{\nu}_{C=O} = +15$ cm^{-1}) suggest these compounds to contain the metal centre *N*,*N*′-co-ordinated. On the other hand, on spectroscopic grounds, **7a**, **7b** can be formulated as bimetallic species containing both *N*,*N*′- and *O*,*O*′-co-ordinated dione to MCl_4 fragments ($\Delta\tilde{\nu}_{C=O} = -60$ cm^{-1}).

The two adducts **6a** and **7a** readily interconvert: $[TiCl_4(C_{12}H_6N_2O_2)]$ **6a** adds $TiCl_4$ affording $[(TiCl_4)_2(C_{12}H_6N_2O_2)]$ **7a** and the reaction of **7a** with dione (1 : 1 molar ratio) affords **6a**, eqn. (4). Thus, the diiminic and quinonoid functionalities in the dione possess different basicities: in fact MCl_4 adds primarily to the nitrogen atoms, and the quinonoid functionality reacts only in the presence of a second equivalent of the tetrachloride.



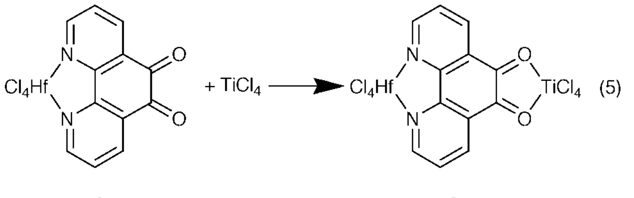
(4)

6a **7a**

Table 2 Redox potentials of 1,10-phenanthroline-5,6-dione and 9,10-phenanthrenequinone in CH_3CN *vs.* SCE

Compound	ε_{1red}/V	ε_{2red}/V	Ref.
1,10-Phenanthroline-5,6-dione	−0.445	−1.251	11
9,10-Phenanthrenequinone	−0.640	−1.220	15

By reaction of $TiCl_4$ with the hafnium derivative **6c** the hetero-bimetallic compound $[Cl_4Hf(C_{12}H_6N_2O_2)TiCl_4]$ **8**, eqn. (5), was obtained. Its IR spectrum shows an intense absorption at 1645 cm^{-1} suggesting the addition of $TiCl_4$ to the quinonoid group. It is interesting that, upon exposure to moist air, the bimetallic derivatives **7** readily produce **6**, the latter being slowly decomposed by moisture. This behaviour is reminiscent of the 1 : 1 complex between $TiCl_4$ and 9,10-phenanthrenequinone[12] which quickly loses the quinone on exposure to moisture, and of $[TiCl_4(phen)]$[13] which is stable in air for at least 30 min.



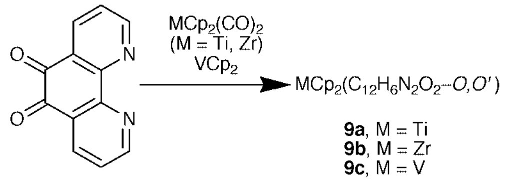
(5)

6c **8**

Reaction of 1,10-phenanthroline-5,6-dione with bis(cyclopentadienyl) derivatives of titanium(II), zirconium(II) and vanadium(II)

Structural and electrochemical[11,14] properties of the dione suggest that its reactivity could be similar to that of 1,10-phenanthroline and 9,10-phenanthrenequinone. In particular, its redox properties are similar to those of 9,10-phenanthrenequinone:[15] both compounds exhibit two reversible voltammetric waves at about −0.5 and −1.2 V (*vs.* SCE in CH_3CN), due to the mono- and bi-electronic reductions of the quinonoid functionality (Table 2).

The reactions of bis(cyclopentadienyl) carbonyl derivatives of titanium(II) or zirconium(II) $[MCp_2(CO)_2]$ or VCp_2 with the dione afford compounds of general formula $MCp_2(C_{12}H_6N_2O_2)$ (M = Ti **9a**, Zr **9b** or V **9c**), eqn. (6). IR spectra of **9a**–**9c** are quite informative about the nature of the compounds. The spectra (polychlorotrifluoroethylene) of **9b** and **9c** show an intense absorption at about 1380 cm^{-1} (**9b**, 1377; **9c**, 1381 cm^{-1}), while the spectrum of **9a** is characterized by a strong absorption at 1429 cm^{-1}. By taking into consideration that bands between 1500 and 1400 cm^{-1} are typical of semiquinonate ligands[16] and absorptions between 1400 and 1300 cm^{-1} characterize a fully reduced quinonoid functionality,[16] we propose that the titanium derivative **9a** is formally a titanium(III) compound containing a phenanthrolinesemiquinonato ligand while the zirconium and vanadium derivatives, **9b** and **9c**, contain the metal in formal oxidation state +IV, analogous to the 9,10-phenanthrenequinone derivatives[17b,c] containing the *O*,*O*′-co-ordinated MCp_2 fragments.



$\longrightarrow MCp_2(C_{12}H_6N_2O_2\text{-}O,O')$ (6)

9a, M = Ti
9b, M = Zr
9c, M = V

The vanadium derivative **9c** is paramagnetic with an effective magnetic moment of 1.86 μ_B at room temperature, typical of a

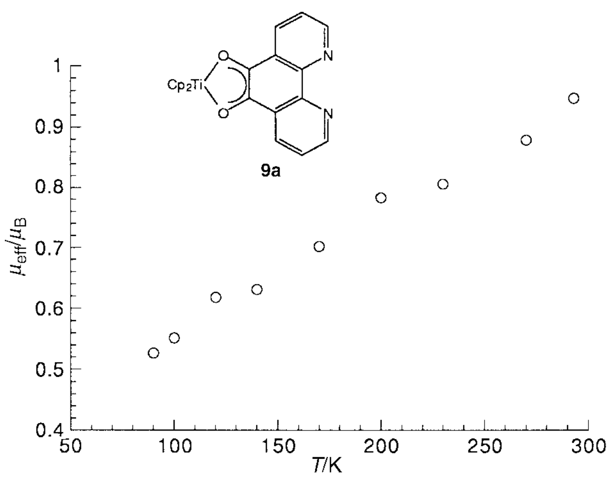


Fig. 4 Plot of μ_{eff} for $[TiCp_2(C_{12}H_6N_2O_2)]$ **9a** as a function of the temperature.

compound containing a vanadium(IV) ion of d^1 electronic configuration. The magnetic properties of **9a** deserve some comments: it is paramagnetic with magnetic moment of *ca.* 0.9 μ_B at 293 K. This value appears in contrast with the results obtained for the analogous 9,10-phenanthrenesemiquinonate derivative of $TiCp_2$[17a] which is diamagnetic, thus suggesting antiferromagnetic coupling between the titanium(III) centre and the 9,10-phenanthrenesemiquinonato ligand. A similar situation is encountered in many organometallic derivatives containing semiquinonato ligands: they exhibit antiferromagnetic coupling resulting in reduced magnetic moments or even in diamagnetism.[18] The difference between **9a** and the 9,10-phenanthrenesemiquinonate of $TiCp_2$ is probably related to the presence of the nitrogen atoms in the condensed aromatic rings of the former, whose electronic effect prevents the complete antiferromagnetic coupling of the two unpaired electrons. In an attempt to clarify this assumption, magnetic measurement on compound **9a** has been carried out at variable temperatures (from 90 to 293 K). As it appears from Fig. 4, the effective magnetic moment gradually increases with temperature: this behaviour can be explained by considering that a triplet–singlet equilibrium is operating, depending on the pairing energy and the energy difference between the HOMO and the LUMO. Since the magnetic moment increases with temperature with values between 0.5 and 1.0 μ_B, it can be deduced that the ground state for the two-electron system titanium(III)/semiquinonato in **9a** is a singlet and the observed paramagnetism is due to the thermal population of the higher triplet state. The value $J = 36.1$ cm^{-1} has been obtained by fitting the experimental data with a Maxwell–Boltzmann distribution for the magnetic moments, thus suggesting weak interactions between the titanium(III) centre of d^1 electronic configuration and the semiquinonato radical anion.‡

Dinuclear compounds containing $C_{12}H_6N_2O_2$

When $[TiCp_2(CO)_2]$ was treated with the dione in a 2 : 1 molar ratio the bimetallic compound $[(TiCp_2)_2(C_{12}H_6N_2O_2)]$ **10** (Scheme 1) was obtained. By following the disappearance of the CO stretching vibrations typical of $[TiCp_2(CO)_2]$ at 1968 and 1884 cm^{-1}, it has been observed that the dione promptly reacts with the first equivalent of $[TiCp_2(CO)_2]$ and that an increase of the reaction temperature (refluxing toluene) is necessary in order to obtain **10** in a quantitative way. We can therefore argue that the formation of **10** is a two-step process consisting of a fast formation of the *O,O′*-co-ordinated titanium(III) derivative **9a**, followed by a thermally induced decarbonylation of $[TiCp_2(CO)_2]$ by **9a**.

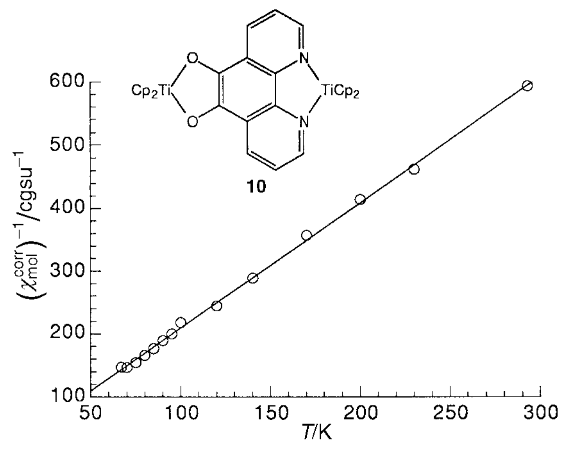
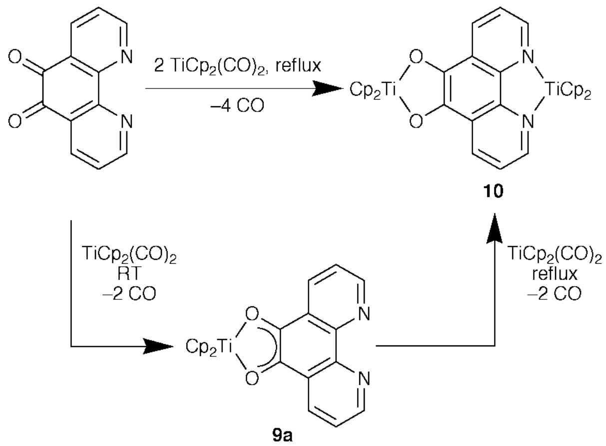


Fig. 5 Plot of $1/\chi_m^{corr}$ for $[(TiCp_2)_2(C_{12}H_6N_2O_2)]$ **10** as a function of the temperature.



Scheme 1

The IR spectrum of compound **10** shows an intense absorption at 1385 cm^{-1} and the absence of strong bands between 1500 and 1400 cm^{-1}. This observation suggests that **10** contains a bielectronically reduced quinonoid functionality. Owing to the fact that we have observed that *N,N′*-co-ordination to **9a** promotes the oxidation of the *O,O′*-co-ordinated titanium(III) centre, see above, we propose that **10** may contain a Cp_2Ti^{IV} fragment co-ordinated to the quinonoid functionality and be described as the reaction product of the formally substituted phenanthroline derivative **9a** with $[TiCp_2(CO)_2]$.

Compound **10** and $[TiCp_2(phen)]$, as obtained from phen and $[TiCp_2(CO)_2]$, are paramagnetic with effective magnetic moments of 2.01 and 1.82 μ_B at 298 K. Variable temperature magnetic susceptibility measurements carried out between 70 and 293 K have shown a Curie–Weiss dependence of χ_M^{corr} on temperature, with Weiss temperatures of −4.7 and −46.5 K, respectively, see Fig. 5. In conclusion, we may suggest that the paramagnetism of **10** and $[TiCp_2(phen)]$ is due to the reduction of the diiminic functionality of the dione or phenanthroline by titanium(II). In this connection it is noteworthy that EPR studies carried out on $[TiCp_2(bipy)]$ have shown the compound formally to contain a titanium(III) centre *N,N′*-co-ordinated to a bipyridyl radical anion.

Reaction of $MCp_2(C_{12}H_6N_2O_2)$ (M = Ti, Zr, V) with $M'Cl_4$ (M′ = Ti or Hf)

The compound $M'Cl_4$ (M′ = Ti or Hf) adds to the diiminic functionality of $C_{12}H_6N_2O_2$ *O,O′*-co-ordinated to the MCp_2

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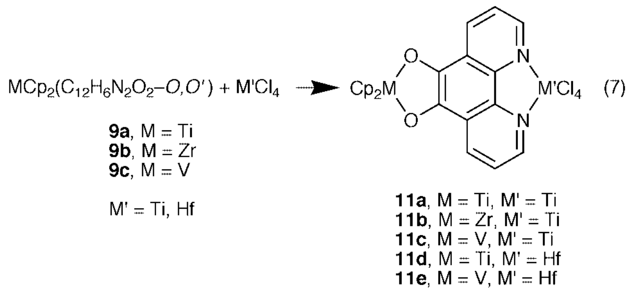
‡ The exchange coupling constant *J* shows values in the range 1–10 and 300–500 cm^{-1} for weakly and strongly interacting paramagnetic ions, respectively.[19]

Table 3 The CO stretching vibrations in [$Cp_2M(C_{12}H_6N_2O_2)M'Cl_4$] **11a**–**11e** derivatives

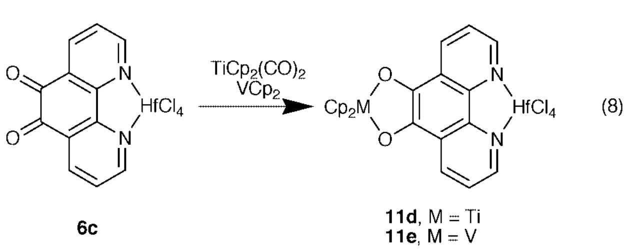
Compound	$\tilde{\nu}_{CO}/cm^{-1}$
11a [$Cp_2Ti(C_{12}H_6N_2O_2)TiCl_4$]	1366
11b [$Cp_2Zr(C_{12}H_6N_2O_2)TiCl_4$]	1375
11c [$Cp_2V(C_{12}H_6N_2O_2)TiCl_4$]	1376
11d [$Cp_2Ti(C_{12}H_6N_2O_2)HfCl_4$]	1383
11e [$Cp_2V(C_{12}H_6N_2O_2)HfCl_4$]	1377



fragment (M = Ti, Zr or V) affording bimetallics of general formula $Cp_2M(C_{12}H_6N_2O_2)M'Cl_4$ **11a**–**11e**, eqn. (7). Their IR spectra are similar and show a strong absorption at about 1370 cm^{-1} (Table 3) suggesting $C_{12}H_6N_2O_2$ is present as its dianion. Since the precursor [$TiCp_2(C_{12}H_6N_2O_2)$] **9a** formally contains a titanium(III) centre and the ligand $C_{12}H_6N_2O_2$ is present as semiquinonate, it is remarkable that the derivatives [$Cp_2Ti(C_{12}H_6N_2O_2)M'Cl_4$] (M′ = Ti **12a** or **12d**) contain the dianion $[C_{12}H_6N_2O_2]^{2-}$ and the titanium centre of the $TiCp_2$ fragment in the formal oxidation state +IV. This clearly suggests that the addition of the $M'Cl_4$ fragment to [$Ti^{III}Cp_2(C_{12}H_6N_2O_2)$] has promoted the formal oxidation of titanium from +III to +IV. This phenomenon is not surprising: electrochemical studies[11] on $C_{12}H_6N_2O_2$ have revealed that mono- and bi-electronic reductions of it in the presence of bivalent cations occur at lower potentials, due to the interaction of the cation with nitrogen atoms. Therefore, we conclude that the co-ordination of the $M'Cl_4$ (M = Ti or Hf) fragment to the nitrogen atoms of [$TiCp_2(C_{12}H_6N_2O_2)$] **9a** makes $C_{12}H_6N_2O_2$ behave as a stronger oxidant.

The presence of the $M'Cp_2$ fragment bonded to the oxygen atoms of the dione reduces the Lewis basicity of the nitrogen atoms. The reactions of the dione with MCl_4 are fast independently of the nature of the tetrahalide ($TiCl_4$ is used in solution, whereas zirconium and hafnium tetrachloride are added as solids to the dione solution). On the other hand, [$MCp_2(C_{12}H_6N_2O_2)$] **9a**–**9c** react with $TiCl_4$ at room temperature, while the addition of $HfCl_4$ to the nitrogen atoms of **9a**–**9c** requires refluxing conditions. This may be due to the fact that *O*,*O*′-co-ordinated $C_{12}H_6N_2O_2$ (in **9a**–**9c**) possesses a reduced Lewis basicity with respect to the "free" ligand and heating is necessary to make the fragmentation of the polynuclear $HfCl_4$ occur.

Magnetic measurements on this class of compounds are consistent with the spectroscopic evidence. The compounds $Cp_2V(C_{12}H_6N_2O_2)MCl_4$] (M′ = Ti **11c** or Hf **11e**) exhibit paramagnetism due to one unpaired electron (**11c**, 1.94; **11e**, 2.04 μ_B), which well corresponds to a system in which the vanadium(IV) ion is surrounded by a diamagnetic environment. On the other hand, [$Cp_2Ti(C_{12}H_6N_2O_2)HfCl_4$] **11d** is diamagnetic, in agreement with $HfCl_4$-promoted electron transfer from titanium(III) to the semiquinonato ligand (see above). The bimetallic compounds **11d**, **11e** can also be obtained by treating bis-cyclopentadienyl derivatives of titanium(II) and vanadium(II) with [$HfCl_4(C_{12}H_6N_2O_2)$] **6c**, eqn. (8). In agreement with the results described above, the reaction of **6c** with [$TiCp_2(CO)_2$] affords a titanium(IV) derivative **11d** showing the increased oxidation power of the quinonoid functionality in **6c** with respect to that of free $C_{12}H_6N_2O_2$.



Conclusion

The aim of this paper was the study of the properties of 1,10-phenanthroline-5,6-dione, including its ligating power towards early transition elements.

This paper has shown that the dione is an interesting starting material for the synthesis of mono- and bi-metallic compounds. The presence of two chelating functionalities and their peculiar reactivity (redox or formation of Lewis adducts) toward Group 4 metal complexes in low or high oxidation states allow the design of step-by-step syntheses of bimetallic compounds.

In addition, due to the presence of hybridized sp^2 nitrogen and oxygen atoms in the same molecule, the dione has allowed the Lewis basicity of the two sets of donor atoms to be compared. The observed formation of a primary *N*,*N*′-co-ordinated adduct, **6**, by reaction of the dione with MCl_4, M = Ti, Zr or Hf, and its subsequent reaction with a second molecule of the tetrahalide to give the binuclear adducts, **7**, clearly indicates that the diiminic functionality is the site of stronger Lewis basicity. This conclusion is also supported by the fact that 1,10-phenanthroline adducts of transition metals are quite common and have been known for many years,[20] while simple acid–base adducts of quinones are rarer.[12]

Work is in progress in order to extend the study to the synthesis and characterization of polynuclear derivatives containing 1,10-phenanthroline-5,6-dione.

Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon, using Schlenk-tube techniques. Solvents were dried by conventional methods prior to use.

IR spectra were recorded with a FT-1725X instrument on Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air, using KBr windows, or on solutions using 0.1 mm path cells (CaF_2 windows). ^1H NMR (200 MHz, TMS as reference) spectra were measured on a Varian Gemini 200BB instrument. Magnetic susceptibilities were measured with a magnetic balance (balance Sartorius 4104, electromagnet Varian V 2900) according to the Faraday method (using $CuSO_4{\cdot}5H_2O$ as reference) at three different field strengths (9400, 10200, 10800 G) and averaging the observed values. Diamagnetic corrections were calculated using Pascal contributions.[21]

The compound $TiCl_4$ (Merck) was distilled and used as a solution in heptane; $ZrCl_4$ (Fluka) and $HfCl_4$ (Cezus Chemie) were treated with boiling $SOCl_2$, the solutions partially evaporated under reduced pressure, heptane was added to precipitate the metal chloride and the suspensions were filtered and the solids dried *in vacuo*. The compounds $[MCp_2(CO)_2]^{22}$ (M = Ti or Zr) and $VCp_2{}^{23}$ were prepared according to literature procedures. 1,10-Phenanthroline (Aldrich) was used without further purification. 1,10-Phenanthroline-5,6-dione was prepared according to a modification of the procedure reported by Yamada *et al.*[8] A mixture of 1,10-phenanthroline (3.65 g, 20.3

Table 4 Crystal data and details of the structure refinement for 1,10-phenantholine-5,6-dione

Empirical formula	$C_{12}H_6N_2O_2$
Formula weight	210.19
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	7.272(10)
b/Å	9.3360(10)
c/Å	13.6050(10)
α/°	83.050(10)
β/°	84.240(10)
γ/°	83.450(10)
Z	4
μ/mm^{-1}	0.108
Reflections collected	3028
Independent reflections	2363 [R(int) = 0.0163]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0436$, $wR2 = 0.1003$

mmol) and KBr (24.85 g, 208.8 mmol) was added to 82 ml of H_2SO_4 (98%) previously cooled at liquid nitrogen temperature. The mixture was slowly allowed to warm to room temperature and a thick orange paste was obtained; then 45 ml of concentrated HNO_3 were added dropwise at room temperature. The resulting red solution was heated at 90 °C for 3 h and then poured into water (1 l). The solution was neutralized with Na_2CO_3 and extracted with CH_2Cl_2. The yellow extract was dried on $MgSO_4$ and the solvent removed *in vacuo*. The orange-yellow solid was recrystallized from EtOH (95%) (2.39 g; 56% yield). It proved to be analytically and spectroscopically pure (IR and ^{1}H NMR).[8]

Crystal structure determination of 1,10-phenanthroline-5,6-dione

Crystal data and details of the structure refinement are reported in Table 4. The crystals (orange prisms) were obtained by slow evaporation of a dichloromethane solution. One of them was selected in air and glued at the end of a glass fibre. The measurements were carried out on a Siemens P4 four-circle diffractometer, equipped with graphite-monochromatized Mo-Kα radiation. Before merging the redundant set of data was corrected for Lorentz-polarization effects but not for absorption owing to the low absorption coefficient. The structure solution was obtained by means of the standard direct methods contained in the TREF procedure of the SHELXTL program[24] and completed by the usual Fourier transform method. The hydrogen atoms were in part found in the Fourier-difference maps and in part introduced in calculated positions.

CCDC reference number 186/1717.

See http://www.rsc.org/suppdata/dt/1999/4389 for crystallographic files in .cif format.

Reactions

$C_{12}H_6N_2O_2$ with MCl_4 (M = Ti, Zr or Hf). *(1 : 1 molar ratio).* Only the procedure for M = Ti is reported, procedures for M = Zr and Hf differing in the fact that the solid metal tetrachlorides were added to the dione solution. A 0.237 M solution of $TiCl_4$ in heptane (4.50 ml, 1.07 mmol) was added to a yellow solution of $C_{12}H_6N_2O_2$ (225 mg, 1.07 mmol) in CH_2Cl_2 (25 ml). An orange solid formed immediately. The suspension was stirred for 6 h and then filtered; the solid was dried *in vacuo* and identified as [$TiCl_4(C_{12}H_6N_2O_2$-*N*,*N*′) **6a**] (312 mg, 73% yield). Found: C, 35.6; H, 1.3; N, 7.0; Ti, 12.4. $C_{12}H_6Cl_4N_2O_2Ti$ requires C, 36.0; H, 1.5; N, 7.0; Ti, 12.0%. IR (Nujol and PCTFE): $\tilde{\nu}$ cm^{-1} 3100w, 3069w, 1699s, 1612w, 1577s, 1483ms, 1432ms, 1300m, 1262mw, 1209mw, 1124m, 1024m, 937w, 810ms, 726ms, 711ms, 669m, 650w, 601w, 422s and 412s.

[$ZrCl_4(C_{12}H_6N_2O_2$-*N*,*N*′)] **6b**. Yellow solid, 69% yield. Found: Zr, 20.6. $C_{12}H_6Cl_4N_2O_2Zr$ requires Zr, 20.8%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3098w, 3071w, 1700s, 1611w, 1577s, 1483m, 1435ms, 1302m, 1262mw, 1209w, 1123ms, 1024ms, 937w, 810ms, 728s, 710m, 669mw, 651w and 599m.

[$HfCl_4(C_{12}H_6N_2O_2$] **6c**. Pale yellow, 59% yield. Found: Hf, 34.8. $C_{12}H_6Cl_4HfN_2O_2$ requires Hf, 33.8%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3093w, 3069w, 1700s, 1614w, 1577s, 1483ms, 1435s, 1302m, 1262mw, 1209mw, 1124ms, 1023ms, 937w, 810ms, 727s, 711m, 651mw, 598ms and 450m.

1 : 2 molar ratio. Only the procedure for M = Ti is reported, the procedure for M = Zr differing in the fact that the solid metal tetrachloride was added to the dione solution. A 0.237 M solution of $TiCl_4$ in heptane (5.00 ml, 1.19 mmol) was added to a yellow solution of $C_{12}H_6N_2O_2$ (123 mg, 0.586 mmol) in CH_2Cl_2 (25 ml). A pale orange solid formed immediately. The suspension was stirred for 6 h and then filtered; the solid was dried *in vacuo* and identified as [$(TiCl_4)_2(C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)] **7a** (216 mg, 62% yield). Found: C, 23.9; H, 1.0; N, 4.2; Ti, 15.7. $C_6H_3Cl_4NOTi$ requires C, 24.4; H, 1.0; N, 4.8; Ti, 16.2%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3093w, 3071w, 1645s, 1616w, 1574s, 1484m, 1429m, 1348m, 1303m, 1262m, 1216mw, 1134m, 1044m, 937w, 823m, 725s, 710w, 669w, 593m, 457m and 415m.

[$(ZrCl_4)_2(C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′) **7b**. Pale yellow, 71% yield. Found: Zr, 27.6. $C_6H_3Cl_4NOZr$ requires Zr, 27.0%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3093w, 3071w, 1647s, 1616w, 1574s, 1484m, 1429m, 1348m, 1303mw, 1262mw, 1216w, 1134m, 1044m, 937w, 823m, 725ms, 710w, 669w, 593m, 457m and 415m.

[$HfCl_4(C_{12}H_6N_2O_2$-*N*,*N*′)] 6c with $TiCl_4$. A 0.237 M solution of $TiCl_4$ in heptane (1.47 ml, 0.348 mmol) was added to a suspension of [$HfCl_4(C_{12}H_6N_2O_2$-*N*,*N*′)] **6c** (185 mg, 0.349 mmol) in CH_2Cl_2 (25 ml). The orange suspension was stirred for 6 h and then filtered. The solid was dried *in vacuo* and identified as [$HfCl_4(C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)$TiCl_4$] **8** (150 mg, 60% yield). Found: C, 19.5; H, 0.6; Hf, 23.3; N, 4.0; Ti, 6.3. $C_{12}H_6Cl_8HfN_2O_2Ti$ requires C, 20.0; H, 0.8; Hf, 24.8; N, 3.9; Ti, 6.7%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3094w, 3071w, 1615w, 1645s, 1575s, 1485m, 1429ms, 1347m, 1302w, 1262mw, 1216w, 1135m, 1099m, 1046w, 937w, 823ms, 725ms, 710w, 669w, 651m, 496w, 440ms and 405ms.

$C_{12}H_6N_2O_2$ with bis(cyclopentadienyl) derivatives of titanium(II), zirconium(II) [$MCp_2(CO)_2$] (M = Ti or Zr) and vanadium(II) VCp_2 (molar ratio 1 : 1). Only the procedure for M = Ti is reported, the other preparations being analogous. The compound [$TiCp_2(CO)_2$] (441 mg, 1.91 mmol) was added to a yellow suspension of $C_{12}H_6N_2O_2$ (401 mg, 1.91 mmol) in toluene (25 ml). Immediate evolution of gas was observed and a deep green solid formed. The suspension was stirred for 12 h and then filtered. The brown-green solid was dried *in vacuo* and identified as [$TiCp_2(C_{12}H_6N_2O_2$-*O*,*O*′)] **9a** (471 mg, 64%). Found: C, 67.9; H, 4.1; N, 7.0; Ti, 12.6. $C_{22}H_{16}N_2O_2Ti$ requires C, 68.1; H, 4.1; N, 7.2; Ti, 12.4%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3093m, 3081s, 1558m, 1478m, 1445m, 1427s, 1386m, 1343w, 1277w, 1074m, 1067m, 1023m, 931m, 819s, 735ms, 564m and 421m.

[$ZrCp_2(C_{12}H_6N_2O_2$-*O*,*O*′)] **9b**. Brown, 75% yield. Found: C, 61.0; H, 3.7; N, 6.3; Zr, 21.8. $C_{22}H_{16}N_2O_2Zr$ requires C, 61.2; H, 3.5; N, 6.5; Zr, 21.2%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3059m, 3044m, 1602ms, 1582s, 1478ms, 1456s, 1429m, 1377s, 1333w, 1315w, 1262w, 1123m, 1072s, 1040ms, 1019m, 804s, 727s, 646w, 606w, 547w, 459w and 419w.

$VCp_2(C_{12}H_6N_2O_2$-*O*,*O*′)] **9c**. Brown, 82% yield. Found: C, 67.4; H, 4.0; N, 7.0; V, 13.1. $C_{22}H_{16}N_2O_2V$ requires C, 67.5; H, 4.1; N, 7.2; V, 13.0%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3062m, 1602m, 1578ms, 1456s, 1430ms, 1381s, 1325mw, 1295w, 1262mw, 1126s, 1075s, 1041s, 1021m, 947w, 927w, 808s, 738ms, 729w, 669w, 617w, 577w, 503w, 449w and 420m. Magnetic measurement: $\chi_M^{corr} = 1.47 \times 10^{-4}$ cgsu; diamagnetic correction = -2.01×10^{-4} cgsu; μ_{eff} (293 K) = 1.86 μ_B.

[TiCp$_2$(CO)$_2$] with 1,10-phenanthroline. The compound [TiCp$_2$(CO)$_2$] (201 mg, 0.859 mmol) was added to a colourless solution of 1,10-phenanthroline (156 mg, 0.867 mmol) in toluene (20 ml). No evolution of gas was observed at room temperature and the IR spectrum of the solution recorded after 8 h of stirring at room temperature showed that most of the starting dicarbonyl derivative was still present. The mixture was then refluxed for 3 h, the solid filtered off, dried and identified [as TiCp$_2$(phen)]. Found: Ti, 13.0. $C_{22}H_{18}N_2Ti$ requires Ti, 13.4%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3020w, 1618mw, 1582w, 1552w, 1500m, 1455m, 1427m, 1315ms, 1262ms, 1123s, 1059s, 1019s, 799 (vs), 727s, 669s, 650ms and 617ms. Magnetic measurement: $\chi_M^{corr} = 1.40 \times 10^{-3}$ cgsu; diamagnetic correction = -2.48×10^{-4} cgsu; μ_{eff} (293 K) = 1.82 μ_B.

$C_{12}H_6N_2O_2$ with [TiCp$_2$(CO)$_2$] (1 : 2 molar ratio). The compound [TiCp$_2$(CO)$_2$] (333 mg, 1.42 mmol) was added to a yellow suspension of $C_{12}H_6N_2O_2$ (150 mg, 0.714 mmol) in toluene (20 ml). Immediate evolution of gas was observed and a deep green solid formed. The IR spectrum of the solution after 8 h of stirring showed two carbonyl bands at 1968 and 1884 cm^{-1} typical of [TiCp$_2$(CO)$_2$]. On the basis of the molar absorption coefficient of the band at 1968 cm^{-1} (ε = 1637 M^{-1} cm^{-1}) it was established that about 50% of [TiCp$_2$(CO)$_2$] was still in solution. The absorptions of the dicarbonyl precursor disappeared after the mixture was then refluxed for 3 h. The brown suspension was filtered and the solid dried and identified as [(TiCp$_2$)$_2$-($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)] **10** (185 mg, 46% yield, brown-violet). Found: C, 67.4; H, 4.3; N, 4.9; Ti, 17.1. $C_{32}H_{26}N_2O_2Ti_2$ requires C, 67.9; H, 4.6; N, 4.9; V, 16.9%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3089w, 3062w, 1577m, 1563m, 1467m, 1431m, 1385s, 1320mw, 1315mw, 1262mw, 1189mw, 1125m, 1073s, 1040m, 1017m, 973w, 946w, 797s, 768w, 715m, 666w, 644w, 592w, 537w, 446w and 420m.

[MCp$_2$($C_{12}H_6N_2O_2$-*O*,*O*′)] 9a–9c with M′Cl$_4$ (M = Ti, Zr or V, M′ = Ti; M = Ti or V, M′ = Hf). Only the procedure for M = M′ = Ti is reported, the other syntheses being analogous (except for the fact that reactions with HfCl$_4$ require heating of the mixture at the reflux temperature of the solvent). The compound TiCl$_4$ in heptane (0.237 M, 2.48 ml, 0.590 mmol) was added to a deep green suspension of [TiCp$_2$($C_{12}H_6N_2O_2$)] **9a** (228 mg, 0.588 mmol) in CH$_2$Cl$_2$ (20 ml). Immediately a dark solid formed. The suspension was stirred for 12 h at room temperature, then filtered. The solid was dried *in vacuo* and identified as [Cp$_2$Ti($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)TiCl$_4$] **11a** (dark violet, 145 mg, 43%). Found: C, 45.3; H, 2.6; N, 4.9; Ti, 17.0. $C_{11}H_8Cl_2NOTi$ requires C, 45.7; H, 2.8; N, 4.8; Ti, 16.9%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3107w, 1600m, 1580m, 1514mw, 1489mw, 1446ms, 1430s, 1366s, 1261m, 1195mw, 1132s, 1078s, 1046s, 810s, 724s, 669w, 607m, 453w, 426w and 402m.

[Cp$_2$Zr($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)TiCl$_4$] **11b**. Brown, 44% yield. Found: C, 42.0; H, 2.3; N, 4.5; Ti, 7.3; Zr, 14.0. $C_{22}H_{16}Cl_4N_2O_2TiZr$ requires C, 42.5; H, 2.6; N, 4.5; Ti, 7.7; Zr, 14.7%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3089w, 1596m, 1583m, 1515w, 1484w, 1452m, 1429ms, 1375s, 1262m, 1132s, 1077s, 1045s, 812s, 726s, 694w, 616m, 414w and 407m.

[Cp$_2$V($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)TiCl$_4$] **11c**. Brown, 75% yield). Found: C, 45.6; H, 2.9; N, 4.8; Ti, 8.2; V, 8.8. $C_{22}H_{16}Cl_4N_2O_2$-TiV requires C, 45.5; H, 2.8; N, 4.5; Ti, 8.2; V, 8.8%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3080m, 1596m, 1582m, 1485w, 1429ms, 1376s, 1319w, 1262ms, 1194w, 1128m, 1077s, 1046s, 811s, 724s, 648w, 602w, 430w, 415w and 402m. Magnetic measurement: $\chi_M^{corr} = 1.60 \times 10^{-3}$ cgsu; diamagnetic correction = -3.05×10^{-4} cgsu; μ_{eff} (293 K) = 1.94 μ_B.

[Cp$_2$Ti($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)HfCl$_4$] **11d**. Reaction temperature = 40 °C; brown, 47% yield. Found: C, 36.9; H, 2.2; N, 3.8; Ti, 6.8; Hf, 25.2. $C_{22}H_{16}Cl_4HfN_2O_2Ti$ requires C, 37.3; H, 2.3; N, 4.0; Ti, 6.8; Hf, 25.2%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3100w, 1614m, 1578m, 1461s, 1415s, 1383s, 1262s, 1191m, 1131s, 1089s, 1077s, 1044s, 812s, 725m, 669w, 641w, 451w, 427w and 404w. Magnetic measurement: $\chi_M^{corr} = -3.93 \times 10^{-4}$ cgsu; diamagnetic correction = -3.33×10^{-4} cgsu.

[Cp$_2$V($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)HfCl$_4$] **11e**. Reaction temperature = 40 °C; brown, 82% yield). Found: C, 36.9; H, 2.1; N, 3.8; V, 7.1; Hf, 25.1. $C_{22}H_{16}Cl_4HfN_2O_2V$ requires C, 37.1; H, 2.2; N, 3.9; V, 7.2; Hf, 25.1%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3102w, 1614m, 1587m, 1464ms, 1431ms, 1377s, 1262m, 1129w, 1094s, 1078s, 1048s, 862m, 808s, 725ms, 641w, 602w, 455m, 427w and 403w. Magnetic measurement: $\chi_M^{corr} = 1.75 \times 10^{-3}$ cgsu; diamagnetic correction = -3.24×10^{-4} cgsu; μ_{eff} (293 K) = 2.04 μ_B.

[HfCl$_4$($C_{12}H_6N_2O_2$-*N*,*N*′)] 6c with VCp$_2$ or [TiCp$_2$(CO)$_2$]. Only the procedure for [TiCp$_2$(CO)$_2$] is reported, the other being analogous. The compound [TiCp$_2$(CO)$_2$] (100 mg, 0.428 mmol) was added to a suspension of [HfCl$_4$($C_{12}H_6N_2O_2$-*N*,*N*′)] **6c** (228 mg, 0.430 mmol) in CH$_2$Cl$_2$ (20 ml). Immediate evolution of gas was observed and a solid formed. The suspension was stirred for 12 h and then filtered. The solid was dried *in vacuo* and identified as [Cp$_2$Ti($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)HfCl$_4$] **11d** (green-brown, 153 mg, 50% yield). Found: Ti, 6.9; Hf, 25.6%. IR (Nujol and PCTFE) as above.

[Cp$_2$V($C_{12}H_6N_2O_2$-*N*,*N*′,*O*,*O*′)HfCl$_4$] **11e**. Brown, 78% yield. Found: V, 7.1; Hf, 25.1%. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3078w, 1601m, 1576ms, 1456ms, 1431ms, 1386s, 1313w, 1262mw, 1194w, 1122ms, 1094s, 1078s, 1046s, 821s, 809ms, 723ms, 669m, 650m, 593m, 449m and 420ms. Magnetic measurement: $\chi_M^{corr} = 1.77 \times 10^{-3}$ cgsu; μ_{eff} (293 K) = 2.05 μ_B.

Acknowledgements

The authors wish to thank the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST, Roma), Programma di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento MURST 1998–1999 for financial support.

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Paper 9/06016B