N,*N*′-Diphenylguanidinato complexes of ruthenium, osmium and iridium*

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N,*N*′-Diphenylguanidine reacted with the hydrido complexes $[MH_2(CO)(PPh_3)_3]$ (M = Ru or Os) and *mer*-$[IrH_3(PPh_3)_3]$ in boiling toluene to afford the complexes $[MH\{PhNC(NH_2)NPh\}(CO)(PPh_3)_2]$ and $[IrH_2\{PhNC(NH_2)NPh\}(PPh_3)_2]$ in which the *N*,*N*′-diphenylguanidinate anions adopt a symmetrical chelate co-ordination mode. Under similar conditions the trifluoroacetato complexes $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ afforded salts $[M\{PhNC(NH_2)NPh\}\{PhNC(NH_2)NPh{\cdot}H\}(CO)(PPh_3)_2][O_2CCF_3]$ containing one chelate *N*,*N*′-diphenylguanidinate anion and one monodentate *N*,*N*′-diphenylguanidine ligand. Spectroscopic evidence indicates that the trifluoroacetate anions are hydrogen bonded to one or more of the N-bound hydrogens.

Guanidine and its N-alkyl or N-aryl analogues are amongst the strongest known organic bases (guanidinium, $pK_a = 13.65$)[2] and as such as usually encountered in co-ordination chemistry as guanidinium counter cations or as neutral N-bonded guanidine ligands.[3] Examples of guanidinate metal complexes were, until recently, unknown. Even now there are, to the best of our knowledge, only six reported examples of transition-metal complexes containing co-ordinated guanidinate anions: the chelate triphenylguanidinato complexes $[Rh(C_5Me_5)\{\eta^2\text{-}PhNC(NHPh)NPh\}Cl]$ and $[Ru(MeC_6H_4Pr^i\text{-}p)\{\eta^2\text{-}PhNC(NHPh)NPh\}Cl]$,[4] the guanidinate-bridged species $[Pt_2(terpy)_2\{\mu\text{-}\eta^2\text{-}NHC(NH_2)NH\}][ClO_4]_3{\cdot}H_2O$(terpy = 2,2′:6′,2″-terpyridine),[5,6] and the triphenylguanidinate-bridged species $[Mo_2\{\mu\text{-}\eta^2\text{-}PhNC(NHPh)NPh\}_4][BF_4]_n$ (n = 0, 1 or 2).[7]

Given that guanidine, $NH_2C(=NH)NH_2$ is the amidine of carbamic acid, $NH_2C(O)OH$, it appears logical to extend our recent study[8–11] of complexes containing the co-ordinated *N*,*N*′-diphenylamidinate anions, $PhNC(R)NPh^-$ (R = H, Me, Et or Ph) to include the synthesis and characterisation of related complexes containing the co-ordinated *N*,*N*′-diphenylguanidinate anion $PhNC(NH_2)NPh^-$. We now describe reactions between *N*,*N*′-diphenylguanidine and some platinum metal hydrides and trifluoroacetates leading to the isolation and characterisation of five complexes containing the co-ordinated *N*,*N*′-diphenylguanidinate anion. These are the first examples of complexes in which *N*,*N*′-disubstituted guanidinate anions function as ligands.

Experimental

N,*N*′-Diphenylguanidine was obtained from the Aldrich Chemical Co. and used as supplied. Other reagents, experimental techniques and instrumentation were as described in a previous paper.[12] Spectroscopic data are given in Table 1.

Preparations

All products described were isolated and purified by a standard procedure. The crude reaction solutions, after cooling to ambient temperature, were filtered and then concentrated under reduced pressure to leave oils. These were crystallised from CH_2Cl_2–MeOH to afford the pure products.

$[RuH\{\eta^2\text{-}PhNC(NH_2)NPh\}(CO)(PPh_3)_2]$. Carbonyldihydridotris(triphenylphosphine)ruthenium (0.6 g, 0.65 mmol) and *N*,*N*′-diphenylguanidine (0.54 g, 2.55 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 2.5 h to give a dark yellow-brown solution. Standard work-up gave white microcrystals (0.41 g, 73%), decomp. 170–173 °C (Found: C, 68.95; H, 4.9; N, 4.8. Calc. for $C_{50}H_{43}N_3OP_2Ru$: C, 69.4; H, 5.0; N, 4.85%).

$[Ru\{\eta^2\text{-}PhNC(NH_2)NPh\}\{\eta^1\text{-}PhNC(NH_2)NPh{\cdot}H\}(CO)(PPh_3)_2][O_2CCF_3]$. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.3 g, 0.34 mmol) and *N*,*N*′-diphenylguanidine (0.28 g, 1.32 mmol) were heated under reflux in toluene (30 cm^3) for *ca.* 5 h to give a yellow solution. Standard work-up gave yellow microcrystals (0.19 g, 57%), m.p. 216–218 °C (Found: C, 65.15; H, 4.5; N, 6.75. Calc. for $C_{65}H_{55}F_3N_6O_3P_2Ru$: C, 65.6; H, 4.7; N, 7.05%).

$[OsH\{\eta^2\text{-}PhNC(NH_2)NPh\}(CO)(PPh_3)_2]$. Carbonyldihydridotris(triphenylphosphine)osmium (0.4 g, 0.39 mmol) and *N*,*N*′-diphenylguanidine (0.5 g, 2.36 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 74 h to give a yellow-brown solution. Standard work-up gave pale yellow microcrystals (0.23 g, 62%), decomp. 222–224 °C (Found: C, 62.45; H, 4.4; N, 4.2. Calc. for $C_{50}H_{43}N_3OOsP_2$: C, 62.95; H, 4.5; N, 4.4%).

$[Os\{\eta^2\text{-}PhNC(NH_2)NPh\}\{\eta^1\text{-}PhNC(NH_2)NPh{\cdot}H\}(CO)(PPh_3)_2][O_2CCF_3]$. Carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.35 g, 0.36 mmol) and *N*,*N*′-diphenylguanidine (0.3 g, 1.42 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 7.5 h to give a pale yellow solution. Standard work-up gave pale yellow microcrystals (0.23 g, 60%), m.p. 274–276 °C (Found: C, 60.4; H, 4.3; N, 6.4. Calc. for $C_{65}H_{55}F_3N_6O_3OsP_2$: C, 61.05; H, 4.35; N, 6.55%).

$[IrH_2\{\eta^2\text{-}PhNC(NH_2)NPh\}(PPh_3)_2]$. *mer*-Trihydridotris(triphenylphosphine)iridium (0.4 g, 0.51 mmol) and *N*,*N*′-diphenylguanidine (0.2 g, 0.95 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 5 h to give a yellow-brown solution. Standard work-up gave white platelets (0.28 g, 60%), m.p. 206–208 °C (Found: C, 63.35; H, 4.7; N, 4.5. Calc. for $C_{49}H_{44}IrN_3P_2$: C, 63.35; H, 4.75; N, 4.5%).

Results and Discussion

N,*N*′-Diphenylguanidine was chosen for our initial study of guanidinate anion co-ordination chemistry for two reasons. First the close analogy between the symmetrical *N*,*N*′-diphenylguanidinate anion, $PhNC(NH_2)NPh^-$, and the *N*,*N*′-diphenylamidinate anions, $PhNC(R)NPh^-$ (R = H, Me, Et or Ph), which we have previously shown to be good chelating

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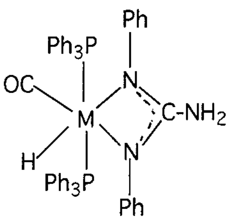
* Dedicated to Geoffrey Wilkinson in affectionate memory.

Complexes of the platinum metals. Part 49.[1]

Table 1 Spectroscopic data

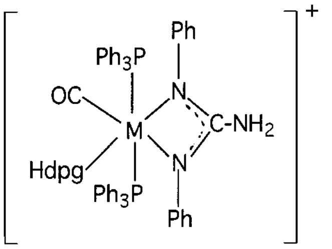
	IR ^{a}/cm^{-1}			NMR (δ, J/Hz)^{b}		
Complex	ν(MH)	ν(CO)	ν(NH)	^{1}H	^{19}F	^{31}P-{^{1}H}
1	2009	1910	3511, 3413	−13.20 (t, $^{2}J_{HP}$ 20, RuH), 3.87 (s, NH_2)	—	47.39 (s)
2	—	1908	3668, 3375, 3335	*c*	−75.44 (s)^{d}	29.6 (s)^{d}
3	2049	1893, 1873 (sh)	3509, 3415	−14.69 (t, $^{2}J_{HP}$ 17, OsH), 3.86 (s, NH_2)	—	20.7 (s)
4	—	1890	3668, 3365, 3335	*c*	−75.41 (s)	−1.12 (s)
5	2220, 2198	—	3441, 3357	−22.69 (t, $^{2}J_{HP}$ 16.8, IrH), 3.66 (s, NH_2)		22.54 (s)
Guanidine				5.44 (s, NH)		

^{a} Nujol mulls. ^{b} In $CDCl_3$ solution, 298 K. Referenced to $SiMe_4$ (^{1}H), external $CFCl_3$ (^{19}F) or external H_3PO_4 (^{31}P). ^{c} δ(NH) not detected. ^{d} Also minor product having δ(F) −76.16, δ(P-{^{1}H}) 35.01 (see text).



I

(M = Ru, Os)



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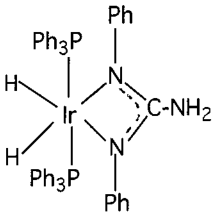

III

ligands,[8,9] and secondly the presence of the functional group (NH_2) on the central carbon atom of the guanidinate ligands offers the promise of some interesting reactivity patterns for future study. The close similarity between the *N*,*N*′-diphenylguanidinate and *N*,*N*′-diphenylamidinate anions is confirmed in the present work by parallels in the stoichiometry, structure and spectroscopic properties of their respective complexes.

[RuH{η^2-PhNC(NH_2)NPh}(CO)(PPh_3)$_2$] 1

This complex was obtained as air-stable white microcrystals from the reaction of *N*,*N*′-diphenylguanidine with [RuH_2(CO)(PPh_3)$_3$] in boiling toluene. The ^{1}H and ^{31}P NMR spectra are indicative of a hydride ligand co-ordinated *cis* to a pair of equivalent triphenylphosphine ligands, and are very similar to those recorded for the closely related amidinato complexes [RuH{PhNC(R)NPh}(CO)(PPh_3)$_2$] which we have previously shown to contain mutually *trans* pairs of triphenylphosphine ligands.[9] We therefore assign a similar *trans*-phosphine stereochemistry **I** (M = Ru) to the *N*,*N*′-diphenylguanidinato complex. The chelate *N*,*N*′-diphenylguanidinate ligand is expected to maximise its resonance stabilisation energy by adopting the symmetric structure shown in **I** rather than the asymmetric alternative PhNC(NHPh)NH. The absence of any evidence for the formation of a second *trans*-phosphine isomer in the case of this complex or its osmium analogue (see below) strongly supports the view that this is indeed the case. The symmetrical chelate ligand structure is also supported by the presence of infrared absorptions at 3413 and 3511 cm^{-1} attributable to the symmetric and asymmetric stretching vibrations of a NH_2 group.

[Ru{η^2-PhNC(NH_2)NPh}{η^1-PhNC(NH_2)NPh·H}(CO)(PPh_3)$_2$][O_2CCF_3] 2

The reaction of the trifluoroacetato complex [Ru(O_2CCF_3)$_2$(CO)(PPh_3)$_2$] with *N*,*N*′-diphenylguanidine in boiling toluene gave the above product as air-stable yellow microcrystals. Analytical data support the proposed stoichiometry and the spectroscopic data are consistent with a salt formulation comprising a complex cation **II** (M = Ru) and a trifluoroacetate counter anion. There is infrared evidence for a hydrogen-bonding interaction between the trifluoroacetate anion and the cation *via* the NH_2 group of the *N*,*N*′-diphenylguanidinate ligand. In particular the ν(N−H) stretching vibrations observed at 3413 and 3511 cm^{-1} for complex **1** are shifted to 3335 and 3375 cm^{-1} for the trifluoroacetate salt **2**. Numerous examples of intermolecular hydrogen bonding between the N-bound protons of guanidines or guanidinium cations and a variety of partners including chloride anions, water or other guanidine molecules have been established by X-ray diffraction methods[13,14] and a similar interaction involving trifluoroacetate anions appears highly reasonable.

The infrared spectrum of complex **2** also displays a ν(N−H) absorption at 3668 cm^{-1} which is absent from the spectrum of complex **1** and which we attribute to the neutral guanidine (Hdpg) ligand. However, in the absence of any other spectroscopic data attributable to this group we are unable to determine its tautomeric form and mode of co-ordination. The absence of any NMR signal attributable to the N-bound protons, and in particular the lack of a signal at *ca.* δ 3.87 similar to the one attributed to the NH_2 group in complex **1** raises the possibility of a rapid fluxional process involving proton transfer between co-ordinated guanidine and guanidinate ligands. Attempts to resolve some of these ambiguities by X-ray diffraction methods have been frustrated to date by poor crystal quality.

Samples of complex **2** displayed additional weak NMR signals [δ(F) − 76.16 (s), δ(P-{^{1}H}) 35.01 (s)] which we tentatively ascribe to the presence of the complex [Ru{η^2-PhNC(NH_2)NPh}(O_2CCF_3)(CO)(PPh_3)$_2$] in very low concentrations.

[OsH{η^2-PhNC(NH_2)NPh}(CO)(PPh_3)$_2$] 3

This air-stable pale yellow microcrystalline product, obtained by the prolonged reaction of *N*,*N*′-diphenylguanidine with [OsH_2(CO)(PPh_3)$_3$] in boiling toluene, is the first example of an osmium guanidinato complex. It displays spectroscopic data consistent with stereochemistry **I** (M = Os). As in the case of the ruthenium analogue the absence of a second *trans*-phosphine isomer provides circumstantial evidence for the symmetrical nature of the guanidinate ligand and this is confirmed by the infrared spectrum which displays absorptions attributable to symmetric and asymmetric ν(N−H) vibrations of an NH_2 group.

[Os{η^2-PhNC(NH_2)NPh}{η^1-PhNC(NH_2)NPh·H}(CO)(PPh_3)$_2$][O_2CCF_3] 4

This complex is obtained in good yield as the sole product from the reaction of *N*,*N*′-diphenylguanidine with [Os(O_2CCF_3)$_2$(CO)(PPh_3)$_2$] in boiling toluene. It displays spectroscopic data consistent with formulation as a salt containing the cation **II** (M = Os) and a trifluoroacetate counter anion, and is therefore a direct analogue of the corresponding ruthenium complex **2**. Like the ruthenium complex it shows infrared evidence for a hydrogen-bonding interaction between the trifluoroacetate anion and the NH_2 group of the co-ordinated guanidinate anion. In particular the symmetric and asymmetric N−H stretching vibrations of the latter are reduced by *ca*. 130 cm^{-1} relative to their values in the non-hydrogen-bonded complex **3**. Again the scarcity of spectroscopic data precludes any firm conclusion concerning the tautomeric form and bonding mode of the neutral *N*,*N*′-diphenylguanidine (Hdpg) ligand. However the presence of an infrared band at 3668 cm^{-1} similar to that observed for the corresponding ruthenium complex suggests an identical structure and mode of co-ordination for the Hdpg ligand in both complexes. Finally the absence of a ^1H NMR signal at *ca*. δ 3.87 attributable to the NH_2 protons of the co-ordinated guanidinate anion raises the possibility of a fluxional process similar to that described for the ruthenium complex **2**.

$[IrH_2\{PhNC(NH_2)NPh\}(PPh_3)_2]$ 5

This product, obtained in good yield as air-stable white platelets from the reaction of *mer*-$[IrH_3(PPh_3)_3]$ with *N*,*N*′-diphenylguanidine in boiling toluene, is the first example of an iridium complex containing a co-ordinated guanidinate anion. The spectroscopic data clearly establish the *cis*-dihydride stereochemistry **III**. Furthermore the spectroscopic equivalence of the two hydride ligands [δ − 22.69 (t), $^2J_{HP}$ 16.8 Hz] offers direct unambiguous evidence for the symmetric nature of the *N*,*N*′-diphenylguanidinate chelate ligand.

Conclusion

The five new *N*,*N*′-diphenylguanidinato complexes described above almost double the number of known examples in which a guanidinate anion is co-ordinated to a transition metal. Their formation in good yield by the direct reaction of *N*,*N*′-diphenylguanidine with platinum-group metal hydrides or trifluoroacetates under relatively moderate conditions suggests that, not withstanding the weak acidity of the parent guanidines, an extensive chemistry of transition-metal guanidinato complexes may be possible and relatively accessible. Moreover, given the biological functions and medicinal properties associated with guanidines and some of their derivatives[15] this area of chemistry may prove of some future significance.

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