Heterodinuclear nitrosyl complexes
Part 3*. New organometallic nitrosyls of iridium(III) and platinum

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Abstract

Treatment of the NO linearly bonded species $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (dppn = 3,6-bis(2′-pyridyl)pyridazine) with X^- anions (X = Cl or I) yields the bent, terminal nitrosyl complexes $[Ir(NO)(X)(dppn)(PPh_3)][PF_6]$. These complexes further react with the organometallic platinum substrates $[PtCl(Me)(dmso)_2]$ (dmso = dimethyl sulfoxide) or [PtI(R)(cod)] (R = Me or Ph, cod = cycloocta-1,5-diene) to give the heterodinuclear derivatives $[(PPh_3)(X)Ir(dppn)(NO)Pt(R)][PF_6]$ (X = Cl, R = Me; X = I, R = Me or Ph). The spectroscopic data suggest the presence of a bridging NO group in the mixed compounds.

Introduction

The bonding modes displayed by the nitrogen monoxide as a ligand in transition metal complexes can be linear, bent or bridging [2]. When nitrosyl compounds further react, electrophilic or nucleophilic attack on the NO group [3], insertions with subsequent formation of C–N bonds [4–8], or changes of its coordination mode are observed.

A process wherein the product results from a two-step reaction (i) linear NO → bent NO and (ii) bent NO → (μ_2-NO) has not been extensively investigated, although few examples of transformations from terminal, linear [4, 9] or bent [10] to bridging NO are reported in the literature.

We have shown in a previous paper [1] that the formation of the mixed species $[(PPh_3)Cl_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PdCl][PF_6]$ is one example of the above mentioned process. We now describe the conversion of a bent, terminal NO group into one which bridges the iridium metal and the organometallic Pt(R) fragment.

Results and discussion

The starting nitrosyl compound, $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (**1**) where dppn is the binucleating ligand 3,6-bis(2′-pyridyl)pyridazine, contains an iridum(I) center which is coordinated in a trigonal bipyramidal geometry with the two PPh_3 molecules in the apical positions. Both dppn, metal-bonded like a 2,2′-bipyridine, and a linear NO (ν(NO) = 1795 cm^{-1}, KBr) lie on the equatorial plane [11]. Complex **1** reversibily reacts with X^- anions yielding the monocationic species $[Ir(NO)(X)(dppn)(PPh_3)_2][PF_6]$ (**2**: X = Cl; **3**: X = I) [12]. In **2** or **3**, the addition of X^- on the dppn and NO plane, promotes the change of the NO bonding mode from linear to bent (ν(NO), KBr: **2** = **3** = 1502 cm^{-1}). Consequently the metal becomes hexacoordinated in an octahedral geometry and is formally oxidised to iridium(III).

New iridium–platinum heterobimetallic species have been prepared in high yields by addition of $[PtCl(Me)(dmso)_2]$, [PtI(Me)(cod)] or [PtI(Ph)(cod)] to the respective chlorinated (**2**) or iodinated (**3**) compounds (1:1 molar ratio in dichloromethane at room temperature). All the binuclear complexes are greenish-yellow, red–brown or brown solids. These solids have been characterised by elemental analysis, spectroscopic techniques (see 'Experimental' and Table 1) as well as by conductivity measurements, which are consistent with 1:1 electrolytes [13] of general formula $[(PPh_3)X_2Ir(dppn)(NO)Pt(R)][PF_6]$ (**4**: X = Cl, R = Me; **5**: X = I, R = Me; **6**: X = I, R = Ph).

In particular, all complexes show a single resonance in the $^{31}P\{^1H\}$ NMR spectrum (at δ −21.37 (**4**), −25.84 (**5**) and −25.18 (**6**) ppm) accounting for an Ir(III)-bonded PPh_3 group. The proton spectra are as expected for a bis-chelate dppn molecule and a

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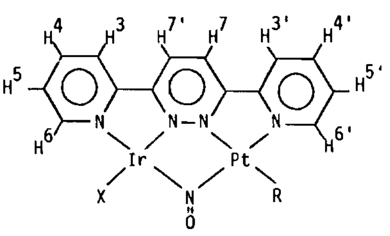
TABLE 1. Proton NMR data (δ (ppm))[a] for the NO-bridged heterodinuclear complexes



Compound		H^6	H^5	H^4	H^3	$H^{6'}$	$H^{5'}$	$H^{4'}$	$H^{3'}$	H^7	$H^{7'}$	Pt–R
4[b, c]	X = Cl; R = Me	8.88	7.68	8.24	8.46	8.56	7.86	d	d	9.22	8.84	1.16[e]
5[f]	X = I; R = Me	9.43	7.81	8.40	8.82	8.75	8.06	8.63	8.82	9.68	9.41	1.21[g]
6[h]	X = I; R = Ph	9.39	7.79	8.39	8.90	8.04	7.94	8.61	8.88	9.78	9.54	7.08, 6.95

[a] All values are relative to $SiMe_4$; in $(CD_3)_2CO$ unless otherwise noted. [b] In CD_3CN. [c] $J(H^6H^5) = 5.0$, $J(H^6H^4) = 1.4$, $J(H^5H^4) = J(H^4H^3) = 7.9$, $J(H^{6'}H^{5'}) = 5.3$, $J(H^{5'}H^{4'}) = 7.1$, $J(H^{5'}H^{3'}) = 1.9$, $J(H^7H^{7'}) = 9.1$ Hz. [d] Multiplet at 8.42–8.41 ppm. [e] $^2J(PtH) = 84.0$ Hz. [f] $J(H^6H^5) = 5.2$, $J(H^6H^4) = 1.4$, $J(H^5H^4) = J(H^4H^3) = 7.9$, $J(H^5H^3) = 1.4$, $J(H^{6'}H^{5'}) = 5.5$, $J(H^{6'}H^{4'}) = 1.5$, $J(H^{6'}H^{3'}) = 1.0$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 7.9$, $J(H^{5'}H^{3'}) = 1.4$, $J(H^7H^{7'}) = 9.1$ Hz. [g] $^2J(PtH) = 81.4$ Hz. [h] $J(H^6H^5) = 5.6$, $J(H^6H^4) = 1.4$, $J(H^5H^4) = J(H^4H^3) = 7.9$, $J(H^5H^3) = 1.3$, $J(H^{6'}H^{5'}) = 5.5$, $J(H^{6'}H^{4'}) = 1.6$, $J(H^{5'}H^{4'}) = J(H^{4'}H^{3'}) = 7.8$, $J(H^{5'}H^{3'}) = 1.2$, $J(H^7H^{7'}) = 9.2$ Hz.

Pt–R moiety (Table 1). Furthermore, in the IR spectra the NO stretching frequency appears at 1476 (**4**) 1460 (**5**) and 1462 (**6**) cm^{-1}, with a lowering of 25–40 cm^{-1} with respect to the parent compounds **2** and **3**. These findings are consistent with the conversion of a bent NO to a bridging one, as found in the formation of $[(PPh_3)Cl_2Ir(\mu\text{-dppn})(\mu\text{-NO})PdCl][PF_6]$ [1]. The mixed Ir(III)/Pd(II) complex has been analysed by X-ray diffraction [1]. Its molecular structure shows that both the dppn and the NO ligands bridge the two metals. In particular, the NO group is bonded in a slightly asymmetric way, the Ir–N and Pd–N bond distances being 2.030(15) and 1.953(17) Å, respectively.

The bond angle Ir–N(O)–Pd is 113.3(7)°, while the distance between the iridium and the palladium centers is 3.327(2) Å. On the basis of these data, the species **4**–**6** are formulated as heterodinuclear dppn- and nitrosyl-bridging complexes as reported in Fig. 1.

The synthesis of **4**–**6** and the NO ligand transformations are summarised in Scheme 1.

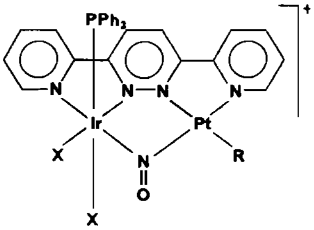


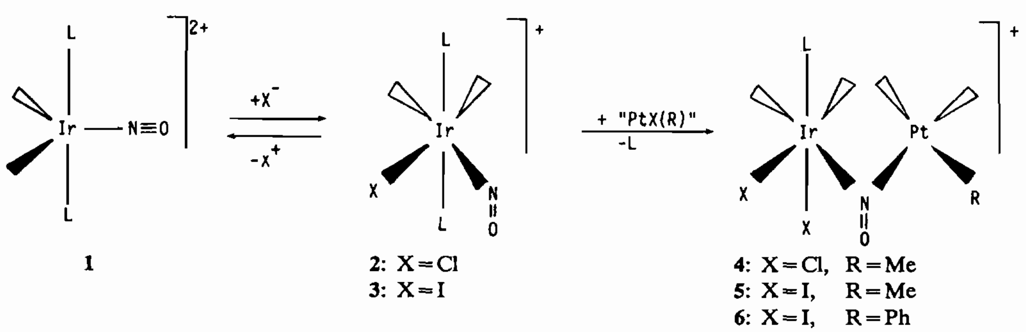
Fig. 1. Proposed geometry for the heterobinuclear complex cations: **4** (X = Cl, R = Me); **5** (X = I, R = Me); **6** (X = I, R = Ph).

Alternatively, complex **5** can be synthesised, albeit in a lower yield, by direct reaction of **1** with [PtI(Me)(cod)] (see 'Experimental'). Moreover, treatment of **1** with $[PtI_2(cod)]$ produces the homologous compound $[(PPh_3)I_2Ir(\mu\text{-dppn})(\mu\text{-NO})PtI][PF_6]$ previously reported [12]. Regarding the reactivity of **1**, **2** or **3** toward organometallic platinum(II) species, it should be pointed out that, in our experimental conditions, none of the above complexes reacted with $[Pt(Me)_2(dmso)_2]$ or $[Pt(Ph)_2(cod)]$. In fact, such a result confirms that the formation of the Ir(III)/Pt(II) heterobimetallic μ_2-NO species requires the migration of an halide ligand from the incoming metal to the iridium center with the dissociation of a PPh_3 molecule (Scheme 1). Therefore, according to the reported data, these syntheses are possible only if the platinum substrate contains at least one halide ligand and yields are improved if a halide anion is first added to **1**.

Experimental

Apparatus and techniques

All reactions were performed under N_2, although the complexes were not air sensitive. The solvents were deoxygenated prior to use. Proton and phosphorus NMR spectra were recorded on a Bruker WH 300 spectrometer. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 1330 spectrometer. Conductivity measurements were performed using a LKB 5300 B conductolyser conductivity bridge. Carbon, H and N analyses were per-



Scheme 1. Synthesis of the heterodinuclear complexes 4–6. The ligand dppn and the anion PF_6^- are omitted for clarity; L is PPh_3.

formed by Mr R. Stillitani, Dipartimento di Chimica, Università della Calabria, Italy.

Preparation of compounds

The ligand 3,6-bis(2′-pyridyl)pyridazine (dppn) [14] was prepared as described; the complexes $[PtCl(Me)(dmso)_2]$ [15], [PtI(Me)(cod)] [16] and [PtI(Ph)(cod)] [16] were prepared by standard methods. The complexes $[Ir(NO)(X)(dppn)(PPh_3)_2][PF_6]$ (X = Cl, I) [12] and $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ [11] were obtained by published procedures.

$[(PPh_3)Cl_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PdCl][PF_6]$ (4)

A colourless solution of $[PtCl(Me)(dmso)_2]$ (0.025 g, 0.062 mmol) in CH_2Cl_2 (3 cm^3) was added to a stirred suspension of $[Ir(NO)(Cl)(dppn)(PPh_3)_2][PF_6]$ (0.072 g, 0.062 mmol) in CH_2Cl_2 (2 cm^3). The resulting green–brown solution turned bright green in a few minutes. After 3 h the green solid formed was filtered out washed with diethyl ether, and vacuum dried. After drying, complex **4** was a greenish-yellow powder (0.050 g, 70%) *Anal.* Found: C, 36.0; H, 2.7; N, 6.4. Calc. for $C_{33}H_{28}Cl_2F_6IrN_5OP_2Pt$: C, 34.6; H, 2.5; N, 6.1%. $\Lambda_m = 88.40\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. ν_{max}(NO) 1476(m) cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR: δ (121.5 MHz, CD_3CN, 273 K, standard 85% H_3PO_4) −21.37(s).

$[(PPh_3)I_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PtMe][PF_6]$ (5)

Method a. A solution of [PtI(Me)(cod)] (0.032 g, 0.072 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred suspension of $[Ir(NO)(I)(dppn)(PPh_3)_2][PF_6]$ (0.090 g, 0.072 mmol) in CH_2Cl_2 (2 cm^3). After 18 h the resulting brown suspension was filtered giving **5**, a red–brown solid (0.057 g, 60%). *Anal.* Found: C, 29.2; H, 2.0; N, 5.1. Calc. for $C_{33}H_{28}F_6I_2IrN_5OP_2Pt$: C, 29.8; H, 2.1; N, 5.3%. $\Lambda_m = 103.20\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. ν_{max}(NO) 1460(m) cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR: δ (121.5 MHz, $(CD_3)_2CO$, 298 K, standard 85%·H_3PO_4) −25.84(s).

Method b. A solution of [PtI(Me)(cod)] (0.015 g, 0.034 mmol) in CH_2Cl_2 (4 cm^3) was added to a solution of $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (0.040 g, 0.034 mmol) in CH_2Cl_2 (2 cm^3) and the resulting brown solution stirred at room temperature for 2 days. The red–brown solid microcrystalline precipitate of **5** formed during this time was filtered and vacuum dried (0.010 g, 24%).

$[(PPh_3)I_2Ir(\mu\text{-}dppn)(\mu\text{-}NO)PtPh][PF_6]$ (6)

The complexes $[Ir(NO)(I)(dppn)(PPh_3)_2][PF_6]$ (0.045 g, 0.035 mmol) and [PtI(Ph)(cod)] (0.018 g, 0.035 mmol) reacted in CH_2Cl_2 (2 cm^3) to give a brown solution. After 12 h a brown precipitate was formed which was collected by filtration, washed with diethyl ether and vacuum dried (0.040 g, 80%). *Anal.* Found: C, 34.3; H, 2.3; N, 5.4. Calc. for $C_{38}H_{30}F_6I_2IrN_5OP_2Pt$: C, 32.8; H, 2.2; N, 5.0%. $\Lambda_m = 75.70\ \Omega^{-1}\ cm^2\ mol^{-1}$ (10^{-3} mol dm^{-3}) in nitromethane. ν_{max}(NO) 1462(m) cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR: δ (121.5 MHz, $(CD_3)_2CO$, 273 K, standard 85% H_3PO_4) −25.18(s).

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