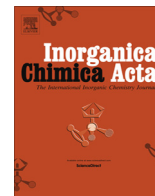




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Research paper

More about the redox behavior of late transition metal triple-decker complexes with cyclo-triphosphorus

 Fabrizia Fabrizi de Biani ^{a,b,*}, Maddalena Corsini ^a, Andrea Ienco ^{c,*}, Maurizio Peruzzini ^c, Fabrizio Zanobini ^c
^a Dipartimento di Biotecnologie Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italy

^b UdR INSTM of Siena, Italy

^c Consiglio Nazionale delle Ricerche – Istituto di Chimica dei Composti Organometallici (CNR ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy

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This work is dedicated to our Friend and Colleague Carlo Mealli, who pioneered the theoretical description of cyclo-P₃ complexes.

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ABSTRACT

The syntheses of the new triple-decker complexes [(triphos)Co(μ,η^{3:3}-P₃)Ru(triphos)](BPh₄)₂; (**CoP₃Ru**) (BPh₄)₂, [(triphos)Co(μ,η^{3:3}-P₃)Os(triphos)](BPh₄)₂; (**CoP₃Os**)(BPh₄)₂ and [(triphos)Ru(μ,η^{3:3}-P₃)Ru(triphos)]PF₆·(CH₃)₂CO; (**RuP₃Ru**)PF₆·(CH₃)₂CO, three new members of the [(tripod)M(μ-P₃)M'(tripod)]ⁿ⁺ (**MP₃M'**) family are described. The structure of the homodinuclear complex (**RuP₃Ru**)PF₆·(CH₃)₂CO is also reported. This latter compound has a structure similar to that of the other members of the series and shows an M···M separation among the longest hitherto found in these compounds. An electrochemical study shows that they are stable in various oxidation states with a VEN value ranging between 28 and 34. A reasoning around the redox data shows a progressive shift of two pairs of redox processes, corresponding to the VEN variation 30/31–31/32 and 32/33–33/34, which almost rigidly moves in the cathode direction as the overall charge of the homoelectronic compound decreases.

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1. Introduction

The interest in white phosphorus coordination chemistry (P₄) was born about fifty years ago when [(PPh₃)₂RhCl(η²-P₄)], the first Rh-P₄ complex was obtained [1]. The *side-on* coordination of the P₄ unit corresponds to its activation and may be followed by different rearrangement of the P₄-tetrahedron resulting into new P_n units (with either n < 4 or > 4) [2]. Alternatively, the tetraphosphorus moiety may undergoes electrophilic attacks forming interesting complexes where new P–C or P-heteroatom units have been assembled [3]. Though the interest in the coordination chemistry of phosphorus with transition metals has been fairly driven by the desire to search for an accessible activation-path of the P₄ molecule, which is of high industrial interest for the production of the many phosphorus-based compounds used in the everyday-life, the particular reactivity of P_n ligands allowed many beautiful and multifaceted molecules to be obtained, which alone would have been enough to keep alive the attention to this fascinating type of chemistry. The activation of P₄ in the coordination sphere

of a transition metal frequently leads to a η³-coordinated cyclo-P₃ unit perfectly isolobal with the cyclopropenilium ion. Indeed in these class of complexes, the cyclo-P₃ system behaves as 3π donor and can form mononuclear sandwich complexes or bridge two metal atom fragments, forming a triple-decker [2,4]. Anyway, both the mononuclear [LM(μ-P₃)]ⁿ⁺ species and the dinuclear triple-deckers [LM(μ-P₃)M'L]ⁿ⁺ may be considered a common feature in the overview of the polyphosphorus coordination chemistry, being practically known for most transition metal ions [5,6]. The great majority of these systems, listed in Table 1, have the general formula [(tripod)M(μ-P₃)]ⁿ⁺, (**MP₃**) from here on) and [(tripod)M(μ,η^{3:3}-P₃)M'(tripod)]ⁿ⁺ (or **MP₃M'**) (tripod = triphos, etriphos, i.e. CH₃C(CH₂PR₂) with R = Ph, Et, Scheme 1) and have been synthesized and characterized by Sacconi et al. in the early '80s [7]. While the mononuclear sandwich complexes follow the classical organometallic 18e⁻ rule, the number of valence electrons (VEN) of all the triple-decker binuclear complexes range between 30 and 34, as previewed by a general theoretical treatment by Hoffmann et al. [8] and successively confirmed by more detailed studies [7,9]. Mealli et al. pointed out the importance of the role played by the P₃ σ bonding network and explicitly addressed the phenomenon that shows how the P–P bond in the ring is weakened by depleting the electron content of the triple-decker,

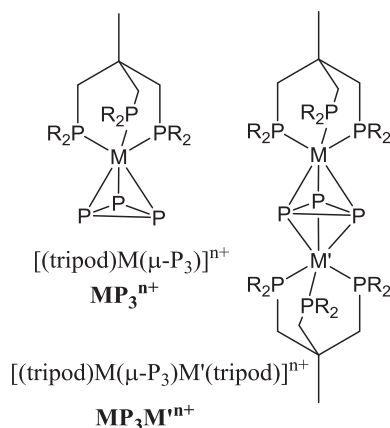
* Corresponding authors at: Dipartimento di Biotecnologie Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italy (F. Fabrizi de Biani).

E-mail addresses: fabrizi@unisi.it (F. Fabrizi de Biani), andrea.ienco@iccom.cnr.it (A. Ienco).

Table 1
Triple-decker complexes [(tripod)M($\mu,\eta^{3:3}$ -P₃)M'(tripod')]ⁿ⁺ with their electron counting.

[(tripod)M($\mu,\eta^{3:3}$ -P ₃)M'(tripod')] ^{n+,a}					
	M	M'	n	VEN	Reference
1	Co	Fe	2	30	[5], b
2	Co	Ru	2	30	This work
3	Co	Os	2	30	This work
4	Ru	Ru	1	30	This work and [9]
5, 6	Co	Co	2	31	[6,7],c
7	Co	Rh	2	31	[7]
8	Co	Ir	2	31	[6]
9	Rh	Rh	2	31	[7]
10, 11	Co	Ni	2	32	[5,7], c
12	Ni	Rh	2	32	[7]
13	Ni	Ni	2	33	[7]
14	Pd	Pd	2	34	[7]

^atripod = tripod' = triphos, except when noted, ^btripod = triphos and tripod' = etriphos, ^cboth symmetrical tripod = tripod' = triphos and asymmetrical tripod = triphos, tripod' = etriphos.



Scheme 1.

while successive electron addition weakens M–P₃ bonds [9]. On the other side, more generally, both the formation and the reactivity of the P₃ ring involve, at least formally, a series of redox processes, for this reason it is surprising that the electrochemistry of these complexes has been practically not yet investigated and only a couple of not extensive reports have been published addressing some preliminary electrochemical properties of nickel and cobalt species. In fact, apart from a couple of pioneering studies on **CoP₃Co²⁺**, **NiP₃Ni²⁺** and **CoP₃** [10,11] as far as we know, no other investigation has been made in this direction. Only recently, the electrochemistry of a couple of new examples of this class of molecules (with different coordinating ligands: [(nacnac)Co($\mu,\eta^{3:3}$ -P₃)Co(nacnac)]^{0,-}; nacnac = β -diketiminato [12] and [(Cp^{'''})Ni($\mu,\eta^{3:3}$ -P₃)Ni(Cp^{'''})]^{0,-}; Cp^{'''} = η^5 -1,2,4-tBu₃C₅H₂ [13]) has been published.

As a contribution to the completeness of the description of these remarkable series of compounds, we report here on the synthesis and characterization of three novel **MP₃M'ⁿ⁺** triple-decker complexes, namely [(triphos)Co($\mu,\eta^{3:3}$ -P₃)Ru(triphos)]²⁺ (**CoP₃Ru²⁺**), [(triphos)Co($\mu,\eta^{3:3}$ -P₃)Os(triphos)]²⁺ (**CoP₃Os²⁺**) and [(triphos)Ru($\mu,\eta^{3:3}$ -P₃)Ru(triphos)]⁺ (**RuP₃Ru⁺**) and discuss their redox properties by comparing them with those of the previously explored compounds [(triphos)Co($\mu,\eta^{3:3}$ -P₃)Co(triphos)]²⁺ (**CoP₃Co²⁺**) and [(triphos)Ni($\mu,\eta^{3:3}$ -P₃)Ni(triphos)]²⁺ (**NiP₃Ni²⁺**). The redox behavior of [(triphos)Ni(η^3 -P₃)]BF₄ (**NiP₃⁺**) is also reported together with that of the previously explored (triphos)Co(η^3 -P₃) (**CoP₃**).

2. Experimental

2.1. Synthesis

All reactions and manipulations were performed under a dry nitrogen or argon atmosphere by using standard Schlenk techniques. The complexes [(triphos)Co(η^3 -P₃)], (**CoP₃**) [14] and [(triphos)Ru(CH₃CN)₃]Otf₂ [15] were prepared as previously reported. Elemental analyses (C, H, N) were performed by using a Carlo Erba model 1106 elemental analyser.

2.2. [(triphos)Co($\mu,\eta^{3:3}$ -P₃)Ru(triphos)](BPh₄)₂; (**CoP₃Ru**)(BPh₄)₂

The complex [(triphos)Ru(CH₃CN)₃]Otf₂ (0.20 mmol, 230 mg) was added as a solid to a stirred orange solution of **CoP₃** (0.20 mmol, 155 mg) in CH₂Cl₂ (50 mL) under nitrogen. The mixture was continuously stirred at room temperature under nitrogen for 10 min and then heated to gentle reflux for 1 h. The color of the solution turned from pale orange to dark violet. Then 20 mL of a solution of NaBPh₄ (0.4 mmol, 140 mg) in acetone and EtOH was added under N₂ with vigorous stirring and a dark violet precipitated was formed after concentrating the solution under N₂. The product was recrystallized from acetone. Elemental analysis calcd (%) for C₁₃₀H₁₁₈B₂CoP₉Ru MW: 2140.7 g mol⁻¹: C 72.93, H 5.55; found C 71.65, H 5.97.

2.2.1. [(P(C₆H₅)₃)₂Os(CH₃CN)₄]Otf₂

Solid Ag(Otf) (7 mmol, 1.8 g) slowly added to stirred yellow solution of (P(C₆H₅)₃)₃OsCl₂ (3.5 mmol, 3.7 g) in CH₃CN (30 mL) in ca. 10 min. After filtering the solid silver chloride which had separated out, the solution heated to reflux and kept at this temperature for 2 h under N₂. The solution was filtered and concentrated up to 10 mL. After adding toluene, a white crystalline precipitated of [(P(C₆H₅)₃)₂Os(CH₃CN)₄]Otf₂ was obtained. Elemental analysis calcd (%) for C₄₆H₄₂F₆N₄O₆OsP₂S₂ MW: 1177.2 g mol⁻¹ C 46.96, H 3.60 N 4.76; found C 47.25, H 3.67, N 4.75.

2.2.2. [(triphos)Os(CH₃CN)₃]Otf₂

The complex [(P(C₆H₅)₃)₂Os(CH₃CN)₄]Otf₂ (0.5 mmol, 64 mg) and triphos (0.5 mmol, 315 mg) was refluxed under N₂ for 5 h in a solution of 2-methoxyethanol (25 mL). The solution was concentrated at 3 mL and 3 mL of CH₃CN and 3 mL of toluene were slowly added. A sticky oil was obtained. After adding more CH₃CN, eventually a white precipitated of [(triphos)Os(CH₃CN)₃]Otf₂ was recovered. The product was washed with a mixture of toluene/CH₃CN (5:1 V/V) and stored under nitrogen. Elemental analysis calcd (%) for C₄₂H₄₁F₆N₃O₆OsP₃S₂ MW: 1145.1 g mol⁻¹ C 44.06, H 3.61 N 3.67; found C 44.13, H 3.68, N 3.62.

2.2.3. [(triphos)Co($\mu,\eta^{3:3}$ -P₃)Os(triphos)](BPh₄)₂; (**CoP₃Os**)(BPh₄)₂

The complex [(triphos)Os(CH₃CN)₃]Otf₂ (0.10 mmol, 120 mg) was added to a stirred solution of **CoP₃** (0.10 mmol, 80 mg) in CH₂Cl₂ (40 mL) under nitrogen. The mixture was stirred at room temperature under nitrogen for 10 min and then heated to reflux for 2 h. The color of the solution slowly turned from pale orange to brown. Then 20 mL of a solution of NaBPh₄ (0.4 mmol, 140 mg) in acetone and EtOH (1:1 V/V) was added under N₂. The solution was further refluxed for 2 h and concentrated to half volume. A dark brown precipitated was obtained. The product was recrystallized from acetone and EtOH (1:1 V/V). Elemental analysis calcd (%) for C₁₃₀H₁₁₈B₂CoOsP₉ MW: 2229.9 g mol⁻¹: C 70.01, H 5.33; found C 69.38, H 5.79.

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