

or a factor of 3.5×10^4 by replacing the flexible PhP-(CH₂CH₂PPh₂)₂ ligand by the *fac*-coordinating MeC(CH₂PPh₂)₃. The origin of this effect is likely the destabilization of the protonated 3H⁺ product by the MeC(CH₂PPh₂)₃ ligand which prevents the complex from achieving the more stable geometry that is accessible with the flexible ligand in 1H⁺ and with monodentate phosphine ligands in 2H⁺. These results establish that it is possible to change substantially the basicities of metal centers by distorting the geometry of a product or reactant with a properly chosen chelating ligand.

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A Highly Reactive Triruthenium Cluster Complex Bearing an Alkyne Coordinated in the μ_3 - η^2 -Perpendicular Mode

Twenty-five years after the pioneering discovery of the first ("unsaturated" alkyne) triiron nonacarbonyl complex, Fe₃(μ_3 - η^2 -RCCR)(CO)₉, by Dahl et al.,¹ we report the first ruthenium compound of a related type.

The unique 46-e iron complex was originally regarded as a curiosity, in that its alkyne moiety was found to lie perpendicular to one metal-metal bond, in sharp contrast to the majority of known ruthenium or osmium complexes that are saturated 48-e species exhibiting a parallel orientation of the alkyne with respect to a metal-metal bond.² The coordination modes of alkynes within trimetallic ensembles were then widely discussed in the literature.³ The perpendicular mode was found of particular interest in account of its proposed implication in the mechanism of carbon-carbon bond cleavage.⁴ Surprisingly, neither the nonacarbonyltriiron complex, nor its rare analogs bearing an alkyne in the perpendicular mode⁵⁻⁷ were found to exhibit the expected behavior of unsaturated species. Furthermore, all attempts to isolate the elusive unsaturated ruthenium derivative "Ru₃(μ_3 - η^2 -RCCR)(CO)₉" remained unsuccessful, thus raising

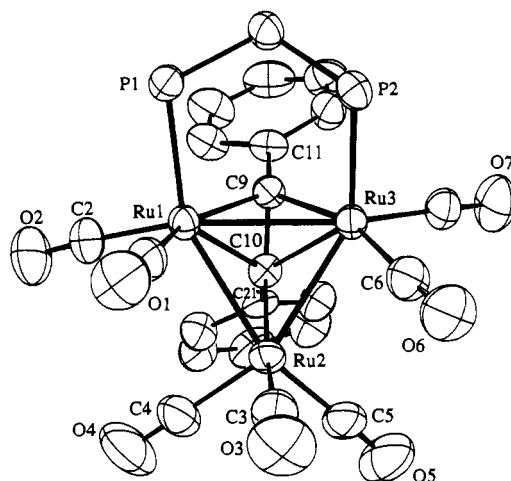
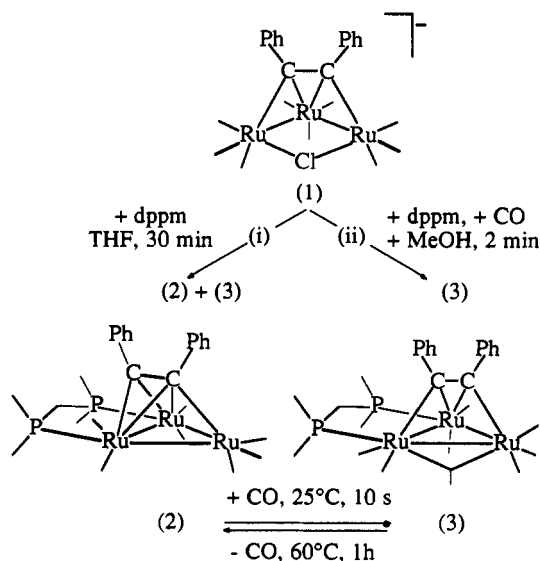


Figure 1. Perspective view of the molecular unit of the complex Ru₃(μ_3 - η^2 -(C₆H₅)CC(C₆H₅))(μ - η^2 -(C₆H₅)₂PCH₂P(C₆H₅)₂)(CO)₇ (2). The four phenyl rings of the bis(diphenylphosphino)methane ligand have been omitted for clarity. Selected interatomic distances (Å) with esd's in parentheses: Ru(1)-Ru(2) = 2.6520 (6), Ru(2)-Ru(3) = 2.6683 (6), Ru(1)-Ru(3) = 2.8120 (7), Ru(1)-P(1) = 2.317 (1), Ru(3)-P(2) = 2.298 (1), Ru(1)-C(9) = 2.108 (4), Ru(3)-C(9) = 2.083 (4), Ru(1)-C(10) = 2.202 (4), Ru(3)-C(10) = 2.265 (4), Ru(2)-C(10) = 2.202 (4), C(9)-C(10) = 1.409 (6).

Scheme 1



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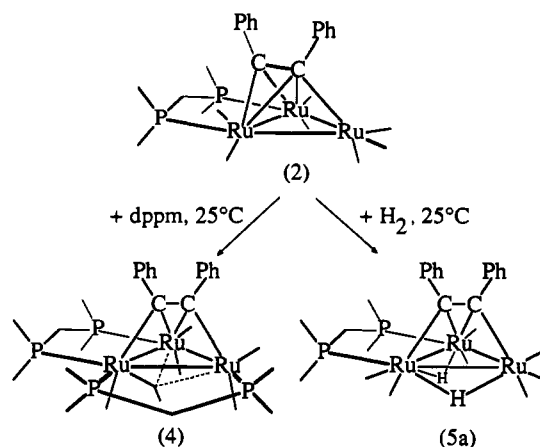
questions about the existence of such a compound.⁸ Besides, the structure of Os₃(μ_3 - η^2 -RCCR)(CO)₉ is still unknown.⁹

Keeping in mind the isolated observation by Smith et al.⁷ that the bis(diphenylphosphino)methane- (dppm-) modified osmium derivative Os₃(μ_3 - η^2 -(C₆H₅)CC(C₆H₅))(μ - η^2 -dppm)(CO)₇ possesses an alkyne coordinated in the perpendicular mode, we were prompted to investigate the effect of phosphine ligands on the anionic species [Ru₃(μ -Cl)(μ_3 - η^2 -RCCR)(CO)₉]⁻, (1) which is readily available via a halide-promoted reaction of alkynes with Ru₃(CO)₁₂.⁸

The reaction of the PPN salt of (1) (PPN = bis(triphenylphosphine)nitrogen cation) with dppm was found to proceed spontaneously in THF solution at 25 °C with concomitant precipitation of (PPN)Cl. We were surprised to observe that even a 2-fold excess of dppm was rapidly consumed, leading to the

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Scheme II



incorporation of four phosphorus donor atoms into the cluster at room temperature (vide infra)! The stoichiometric reaction between PPN(1) and 1 equiv of dppm led to a mixture of two neutral complexes, namely a green compound **2** (a very unusual color for a ruthenium carbonyl cluster) and a violet species, **3**, in approximate ratio 1/10 (Scheme I, path i). In a slightly modified procedure involving the addition of dppm under CO and in the presence of methanol (Scheme I, path ii),¹⁰ we were able to obtain the violet complex **3** selectively within less than 2 min at 25 °C (yield 80–85%, crystallized). The isolated green species could be also cleanly converted into the violet one in contact with CO at 25 °C within about 10 s! The reverse transformation leading to quantitative yields of the green species was achieved within 1 h in refluxing THF under a stream of inert gas.¹⁰ We rapidly realized that we were just observing for the first time the clean and reversible interconversion between an unsaturated alkyne-triruthenium cluster and its CO adduct. The green species was subsequently crystallized and formulated as the 46-e complex $\text{Ru}_3(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\mu\text{-}\eta^2\text{-dppm})(\text{CO})_7$ (**2**), analogous to the above-mentioned osmium derivative.⁷ Its molecular structure is shown in Figure 1.¹¹ It consists of a triangular array of ruthenium atoms, one edge of which is supported by a bridging dppm ligand occupying two pseudoequatorial coordination sites. The diphenylacetylene ligand exhibits the $\mu_3\text{-}\eta^2$ -coordination mode, with the carbon-carbon bond positioned perpendicular to the supported edge Ru(1)–Ru(3). The structural analogies between **2** and the osmium derivative are such that the differences between the respective Ru–C(alkyne) and Os–C(alkyne) bonds are in all cases very close to the esd's.

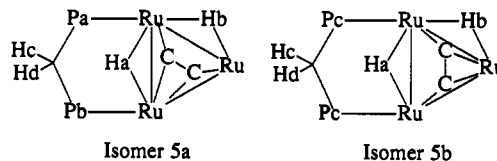
Yet, in spite of these analogies, the two species are not comparable with regard to reactivity. Unlike its osmium analogue, the ruthenium complex is reactive toward CO (Scheme I),

phosphines, and hydrogen (Scheme II), in all cases at 25 °C. The violet CO adduct was formulated as $\text{Ru}_3(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\mu\text{-}\eta^2\text{-dppm})(\mu\text{-CO})(\text{CO})_7$ (**3**).^{10,12} The reaction of **2** with dppm at 25 °C was found to produce the (dppm)₂ derivative $\text{Ru}_3(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\mu\text{-}\eta^2\text{-dppm})_2(\text{CO})_6$ (**4**) (yield 53%),¹³ the X-ray structure of which revealed a parallel orientation of the alkyne.¹⁴ The latter could be alternately obtained directly from the salt PPN(1), as noted above. Finally, the reaction of **2** with hydrogen (1 atm, 10 min, 25 °C) provided the dihydrido complex $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\mu\text{-}\eta^2\text{-dppm})(\text{CO})_7$ (**5**) in 89% yield.¹⁵ An NMR study of the solution at –80 °C revealed the occurrence of two isomers in solution (approximate ratio **5a**/**5b** = 10/1). The X-ray structure of **5a** was determined.¹⁶

In parallel to these observations, we attempted to determine whether the presence of one monodentate phosphine ligand (instead of dppm) on the alkyne-triruthenium framework would be sufficient to stabilize a perpendicular orientation of the alkyne. The answer proved to be negative for triphenylphosphine whose reaction with PPN(1) gave only the saturated 48-e complex $\text{Ru}_3(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\mu\text{-CO})(\text{CO})_8(\text{PPh}_3)$ (**6**),^{17,18} with no evidence for a corresponding unsaturated species.

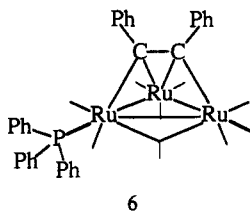
Thus, the incorporation of bis(diphenylphosphino)methane into the ligand shell of an alkyne-triruthenium carbonyl cluster is presently the only way to trap the alkyne in its unstable perpendicular coordination mode and to observe its mobility onto the

- (12) (a) The structure of the corresponding dimethylacetylenedicarbonyl complex has been determined.^{12b} (b) Bruce, M. I. *J. Organomet. Chem.* **1990**, *400*, 321.
- (13) (a) Typical preparative procedure for **4**: a THF solution of **2** (161 mg, 0.152 mmol) and dppm (58 mg, 0.152 mmol) was stirred for 3 h at 25 °C, giving exclusively 114 mg of the red-violet compound **4** crystallized from dichloromethane/hexane as well-defined platelets (yield 53%) (note: **4** is partially altered on a chromatographic column). (b) Spectroscopic data for **4**: IR (CH₂Cl₂) ν 2077 w, 2005 s, 1972 m, 1941 m, 1920 m (C=O) cm⁻¹; ³¹P NMR (250 MHz, CDCl₃) δ 27.8 (m, P₁), $J(\text{P}_1\text{-P}_2) = 18$ Hz; $J(\text{P}_1\text{-P}_3) = 57$ Hz), 22.9 (m, P₂), $J(\text{P}_1\text{-P}_2) = 18$ Hz; $J(\text{P}_2\text{-P}_4) = 82$ Hz), 21.7 (m, P₃), $J(\text{P}_3\text{-P}_4) = 37$ Hz; $J(\text{P}_1\text{-P}_3) = 57$ Hz), 7.5 (m, P₄), $J(\text{P}_3\text{-P}_4) = 37$ Hz; $J(\text{P}_2\text{-P}_4) = 82$ Hz).
- (14) Crystal data for **4**: monoclinic P2₁/n, $a = 21.467$ (4) Å, $b = 15.278$ (2) Å, $c = 22.751$ (4) Å, $\beta = 113.07$ (1)°, $V = 6865$ (2) Å³, $Z = 4$.
- (15) (a) Preparation of **5**: hydrogen gas (1 atm) was bubbled through a dichloromethane solution (20 mL) of **2** (191 mg, 0.180 mmol) at 25 °C for 10 min. The resulting yellow complex **5a** was purified by chromatography and crystallized (171 mg; yield 89%). (b) Spectroscopic and analytical data for **5**: IR (CH₂Cl₂) ν 2085 w, 2055 vs, 2025 s, 1995 vs, 1940 m (C=O) cm⁻¹. Anal. Calcd (found): C, 51.84 (51.93); H, 3.62 (3.22). Two isomers were detected by NMR at –80 °C; they differ in the orientation of the alkyne with respect to the edge-bridging dppm ligand. P and H nuclei are labeled as indicated. Isomer **5a**: ³¹P NMR



- (10) (a) Preparation of **3**: methanol (6 mL) was added under CO (1 atm) to a mixture of the salt PPN(1) (300 mg, 0.229 mmol) and dppm (88 mg, 0.229 mmol) dissolved in 3 mL of dichloromethane. After 2 min, the only resulting complex, **3**, crystallized from the solution. It was filtered, chromatographed on silica gel (dichloromethane/hexane, 1/4), and recrystallized from dichloromethane/methanol (214 mg; yield 86%). (b) Spectroscopic and analytical data for **3**: IR (CH₂Cl₂) ν 2052 m, 2000 vs, 1970 m, 1945 sh, 1830 w, br (C=O) cm⁻¹; ³¹P NMR (200 MHz, CDCl₃) δ 35.0 (s, 2 P). Anal. Calcd (found): C, 51.79 (51.79); H, 2.97 (2.96). (c) Best preparative procedure for **2**: a THF solution of **3** was refluxed for 1 h under a stream of inert gas. After chromatographic purification (dichloromethane/hexane, 1/4), **2** was crystallized from the same solvent mixture (yield 80%). The conversion of **2** into **3** was instantaneous under a CO stream. (d) Spectroscopic and analytical data for **2**: IR (CH₂Cl₂) ν 2055 s, 1987 vs, 1925 m (C=O) cm⁻¹; ³¹P NMR (200 MHz, CDCl₃) δ 40.6 (s, 2 P). The extreme sensitivity of **2** affects the precision of the elemental analysis; best result is as follows. Anal. Calcd (found): C, 51.66 (52.08); H, 3.11 (3.04).
- (11) Crystal data for **2**: monoclinic P2₁/n, $a = 10.958$ (2) Å, $b = 19.224$ (3) Å, $c = 20.340$ (2) Å, $\beta = 100.687$ (9)°, $V = 4210.7$ (9) Å³, $Z = 4$, $\mu(\text{Mo K}\alpha) = 11.66$ cm⁻¹. Data collection was performed at 20 °C on a Enraf Nonius CAD4 instrument. Direct methods (SHELX86) and least-squares refinement were used. $R_w = 0.041$ and $R = 0.033$ for 6328 reflections. Full details are provided in the supplementary material.

- (200 MHz, CDCl₃) δ 17.51 (d, P_a), $J(\text{P}_a\text{-P}_b) = 51$ Hz), 8.38 (d, P_b), $J(\text{P}_a\text{-P}_b) = 51$ Hz). ¹H NMR (200 MHz, CDCl₃) δ 7.5–6.4 (m, 30 H, C₆H₅), 3.04 (m, 2 H, CH₂), $J(\text{H}_c\text{-H}_d) = 13$ Hz, $J(\text{H}_c\text{-P}_b) = J(\text{H}_d\text{-P}_b) = 11$ Hz, $J(\text{H}_c\text{-P}_a) = J(\text{H}_d\text{-P}_a) = 12$ Hz), –14.01 (dd, H_a (μ -hydride), $J(\text{P}_a\text{-H}_a) = 14$ Hz, $J(\text{P}_b\text{-H}_a) = 12$ Hz), –18.89 (d, H_b (μ -hydride), $J(\text{P}_a\text{-H}_b) = 37$ Hz). Isomer **5b**: (tentative assignment) ³¹P NMR (200 MHz, CDCl₃) δ 39.94 (s, 2 P_c). ¹H NMR (200 MHz, CDCl₃) δ 7.5–6.4 (m, 30 H, C₆H₅), 2.27 (dd, H_c, CH₂), $J(\text{H}_c\text{-H}_d) = 13$ Hz, $J(\text{H}_c\text{-P}_c) = 21$ Hz), 3.51 (dd, H_d, CH₂), $J(\text{H}_d\text{-H}_c) = 13$ Hz, $J(\text{H}_d\text{-P}_c) = 22$ Hz), –15.25 (t, H_a (μ -hydride), $J(\text{P}_c\text{-H}_a) = 5$ Hz), –18.76 (t, H_b (μ -hydride), $J(\text{P}_c\text{-H}_b) = 15$ Hz).
- (16) Crystal data for **5a**: monoclinic P2₁/n, $a = 11.165$ (2) Å, $b = 16.281$ (2) Å, $c = 19.920$ (2) Å, $\beta = 96.18$ (1)°, $V = 4263.5$ (9) Å³, $Z = 4$; $R = 0.031$, $R_w = 0.036$.
- (17) (a) Preparation of **6** (simplest procedure): addition of PPh₃ (53 mg, 0.20 mmol) to $\text{Ru}_3(\mu_3\text{-}\eta^2\text{-(C}_6\text{H}_5)_2\text{CC(C}_6\text{H}_5)_2)(\text{CO})_{10}$ (154 mg, 0.20 mmol) in THF (20 mL) at 25 °C, gave 167 mg of complex **6** after 1 h (yield 83%). (b) Spectroscopic and analytical data for **6**: IR (CH₂Cl₂) ν 2072 ms, 2037 vs, 2022 s, 2005 m, 1995 m, 1985 m, 1967 w, sh, 1870 w, br (C=O) cm⁻¹; ³¹P NMR (200 MHz, CDCl₃) δ 36.6 ppm. Anal. Calcd (found): C, 49.50 (49.45); H, 2.36 (2.53).
- (18) Crystal data for **6**: triclinic P $\bar{1}$, No. 2, $a = 12.1372$ (9) Å, $b = 18.115$ (2) Å, $c = 8.900$ (3) Å, $\alpha = 84.89$ (2)°, $\beta = 101.42$ (2)°, $\gamma = 97.325$ (7)°, $V = 1898.3$ (6) Å³, $Z = 2$.



6

trimetallic framework. The present work is also the first demonstration that the unsaturation inherent to the perpendicular mode is not a formalism but is effectively substantiated by chemical reactivity.

Acknowledgment. Financial support of this work by the CNRS is gratefully acknowledged.

Supplementary Material Available: A description of the experimental details for the X-ray structure analysis of complex 2 and tables of crystallographic data, refined atomic coordinates and hydrogen coordinates, anisotropic thermal parameters, interatomic distances, and bond angles (11 pages); a listing of observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Articles

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Catalytic Oxidation of the (Hydroxymethyl)chromium(III) Ion by the Superoxo-chromium(III) Ion

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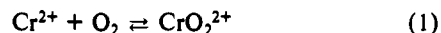
The superoxochromium(III) ion, CrO_2^{2+} , is an efficient catalyst for autoxidation of the (hydroxymethyl)chromium(III) ion, $\text{CrCH}_2\text{OH}^{2+}$, in aqueous solution. The reaction involves one-electron oxidation of $\text{CrCH}_2\text{OH}^{2+}$ by CrO_2^{2+} , $k = 137 \text{ M}^{-1} \text{ s}^{-1}$, to yield Cr^{2+} , CH_2O , and the novel (hydroperoxo)chromium(III) ion, $\text{CrO}_2\text{H}^{2+}$. The Cr^{2+} produced reacts rapidly with O_2 to regenerate the catalyst, CrO_2^{2+} . When oxygen is depleted, the Cr^{2+} reacts instead with CrO_2^{2+} to produce the chromyl(IV) ion, CrO^{2+} . This initiates a chain reaction that rapidly consumes the remaining CrO_2^{2+} and a stoichiometric amount of $\text{CrCH}_2\text{OH}^{2+}$.

Introduction

Molecular oxygen is a powerful oxidant if not always a rapid one. Recent studies of the complexes formed between metal ions and molecular oxygen¹ have shown that coordination and partial reduction activate molecular oxygen toward many organic and inorganic substrates. Such reactions, important both industrially and biologically, involve a number of intermediates, whose lifetime and reactivity depend dramatically on the metal and ligands. Macrocycles, especially porphyrins, have a strong stabilizing effect on such intermediates, and the literature abounds with examples of metal-porphyrin complexes containing oxygen in the superoxo, peroxy, or oxo forms and the metal in any of a number of unusual oxidation states.²

Much less information is available on similar chemistry in non-porphyrin systems, especially in aqueous solution, mostly because the intermediates involved are usually too short-lived to be observed directly. With a few exceptions,^{1,3-5} the work reported in this area deals almost exclusively with oxygen-carrying properties of metal-oxygen adducts,^{1,6} not with mechanistic studies of their electron-transfer chemistry.

The reaction of Cr^{2+} with O_2 yields a long-lived superoxochromium(III) ion,⁷ CrO_2^{2+} (eq 1; here and elsewhere the co-



ordinated water molecules are omitted). CrO_2^{2+} has been identified and characterized as a complex of chromium(III) with superoxide.⁵ Unlike most of the other transition-metal-oxygen adducts, CrO_2^{2+} can be handled at room temperature even under air-free conditions, since the reverse reaction is so slow, $k_{-1} = 2.5 \times 10^{-4} \text{ s}^{-1}$.⁵ This makes it possible to study its chemistry without

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