

Figure 6. Free energy correlation equating the optical energy gap (MLCT, in eV) to the thermodynamic energy gap ($\Delta E_{1/2}$). The numbered entries are as follows: (1) [bpyRu(bpqRu(bpy)₂)₂]⁶⁺; (2) [Ru(bpqRu(bpy)₂)₂]⁶⁺; (3) [(Ru(bpy)₂)₂bpq]⁴⁺; (4) [(bpy)(bpm)(Ru(bpy)₂)₂]⁶⁺; (5) [(Ru(bpy)₂)₂bpm]⁴⁺; (6) [Ru(bpmRu(bpy)₂)₃]⁸⁺; (7) [(Ru(bpy)₂)₃HAT]⁶⁺; (8) [(Ru(bpy)₂)₂HAT]⁴⁺; (9) [Ru(bpy)₂(bpq)]²⁺; (10) [Ru(bpy)(bpq)₂]²⁺; (11) [Ru(bpq)₃]²⁺; (12) [Ru(bpy)₂HAT]²⁺; (13) [Ru(bpy)₂bpm]²⁺; (14) [Ru(bpy)(bpm)₂]²⁺; (15) [Ru(bpm)₃]²⁺. The correlation includes related bpm complexes from ref 2, related bpq complexes from ref 13, and related HAT complexes from ref 26.

correlation between the MLCT energy in electronvolts and $\Delta E_{1/2}$ in volts is linear, the slope is 1.0, and the correlation coefficient is 0.99.

Finally, we would note some properties concerning the stability of oxidized and reduced oligonuclear complexes. Attempts were

made to obtain global n values for oxidation and reduction of the bimetallic, trimetallic, and tetrametallic complexes. The processes were effected electrochemically in acetonitrile at a Pt working electrode. Oxidations were difficult, at best. Apparently, either the oxidized complexes oxidized the solvent, which then formed a film on the electrode, or the oxidized oligomer itself formed a decomposition product that formed a film on the electrode surface. In the case of [Ru(bpmRu(bpy)₂)₃]⁸⁺, the cyclic voltammogram after electrolysis suggested that the oligomer had dissociated into monometallic species. An additional wave located at about $E_{1/2} = 1.41$ V vs SSCE was present, which can be associated with [Ru(bpy)₂(bpm)]²⁺. Reductions, on the other hand, were reversible for studies effected at potentials more positive than -1.0 V vs SSCE. [Ru(bpmRu(bpy)₂)₃]⁸⁺ was reduced by 3 electrons ($n = 3.0$) at -0.7 V, [(bpy)Ru(bpmRu(bpy)₂)₂]⁶⁺ was reduced by 2 electrons ($n = 1.9$) at -0.6 V, and [(Ru(bpy)₂)₂bpm]⁴⁺ was reduced by 2 electrons ($n = 1.9$) at -1.1 V. Each of these reductions was reversible; that is, upon reoxidation of the complexes in solution at zero volts, the required number of coulombs was obtained. The fact that the processes were reversible was verified by cyclic voltammetry. The voltammograms before and after electrolysis were the same.

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Registry No. Ru(bpy)₂Cl₂, 15746-57-3; [Ru(bpy)(bpm)₂](PF₆)₂, 85335-57-5; [Ru(bpy)(bpq)₂](PF₆)₂, 106471-69-6; [Ru(bpq)₃](PF₆)₂, 106222-81-5; [Ru(bpm)₃]Cl₂, 65034-88-0; [Ru(bpy)(bpmRu(bpy)₂)₂](PF₆)₆, 116026-59-6; [Ru(bpmRu(bpy)₂)₃](PF₆)₈, 116209-67-7; [Ru(bpy)(bpqRu(bpy)₂)₂](PF₆)₆, 116052-56-3; [Ru(bpqRu(bpy)₂)₃](PF₆)₈, 116052-54-1.

Supplementary Material Available: A listing of elemental analyses (1 page). Ordering information is given on any current masthead page.

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(Hexamethylbenzene)ruthenium(II) Complexes: Synthesis and Coordination Chemistry of a Novel Tridentate Ligand with an O,O,Cl Donor Set

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Trimethyl phosphite reacts with [(C₆Me₆)RuCl₂]₂ in methanol to yield the cation [(C₆Me₆)RuCl{P(OCH₃)₃}₂]⁺, which has been isolated as a chloride or hexafluorophosphate salt. [(C₆Me₆)RuCl{P(OCH₃)₃}₂]⁺ undergoes a sequence of two Michaelis-Arbuzov type reactions to give the neutral complex [(C₆Me₆)RuCl{P(O)(OCH₃)₂{P(OCH₃)₃}]} and the L⁻ anion [(C₆Me₆)RuCl{P(O)(OCH₃)₂}₂]⁻. Attempts to isolate the anion in the form of its sodium salt NaL have led to products that always contain additional sodium iodide or sodium hexafluorophosphate. The free acid HL can be prepared by protonation from NaL or directly from the reaction of [(C₆Me₆)RuCl₂]₂ with dimethyl phosphonate, HP(O)(OCH₃)₂. L⁻ is a uninegative, potentially bidentate or tridentate ligand with an O,O,Cl donor set. It reacts with many transition-metal and main-group-metal ions, e.g. Mⁿ⁺ = Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Al³⁺, or Fe³⁺, to give 2:1 complexes of the composition [ML₂]⁽ⁿ⁻²⁾⁺. The reactions of the complexes [(ring)MCl₂]₂, (ring)M = (C₅Me₅)Rh, (C₆Me₆)Ru, and (*p*-cymene)Ru, with L⁻ lead to the cationic complexes [(C₅Me₅)RhL]⁺, [(C₆Me₆)RuL]⁺, and [(*p*-cymene)RuL]⁺, which have been isolated as hexafluorophosphate salts. L⁻ also functions as a tridentate O,O,Cl ligand in LRe(CO)₃, which has been prepared from HL and ReBr(CO)₅. HL oxidatively adds to the metal(0) complexes [Mo(CH₃CN)₃(CO)₃] and [W(DMF)₃(CO)₃] to yield metal hydride complexes of the composition [LM(CO)₃H]. The molybdenum hydride is labile and rapidly gives HL and Mo(CO)₆ under an atmosphere of CO gas. The tungsten hydride is unreactive under the same conditions. The copper carbonyl complex LCu(CO) has been prepared in a comproportionation reaction of CuL₂ with copper metal under an atmosphere of carbon monoxide. LCu(CO) is the first neutral complex with a Cu(CO)Cl unit that could be isolated.

Introduction

Polydentate organic ligands with practically all combinations of the donor centers N, O, P, S, As, and Se are well-known, but

chelating ligands with a halogen atom as one of the donor centers are very rare. The coordination chemistry of such ligands is only just emerging.¹ As a rule organic halides seem to be extremely

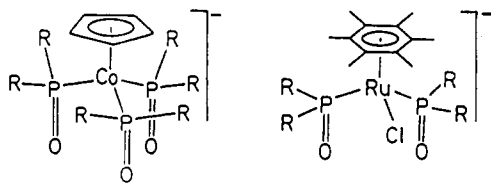


Figure 1. Schematic structures of the O,O,O chelating ligands $[(C_5H_5)Co\{P(O)R_2\}_3]^-$ and the O,O,Cl chelating ligand $[(C_6Me_6)RuCl\{P(O)R_2\}_2]^-$ ($R = OCH_3$).

weak ligands. There are also only a few metal complexes known that can act as multidentate ligands and that have a terminal halogen ligand available as an additional donor center. On the other hand, the tendency of halides to act as bridging ligands between two metal ions is well-known. We became interested in polydentate ligands with a halogen atom as one of the donor centers when we discovered that anionic complexes of the general composition $[(C_5H_5)Co\{P(O)R_2\}_3]^-$ (Figure 1) act as tridentate oxygen ligands. They turned out to be powerful ligands that can coordinate to metal ions in medium and high oxidation states. Furthermore we found that they can stabilize equally well a large variety of low-valent organometallic fragments.²⁻⁴ Most of these organometallic derivatives are surprisingly inert. In order to prepare more reactive analogues, we thought of designing a ligand similar to the tripod ligands $[(C_5H_5)Co\{P(O)R_2\}_3]^-$ but with only two strongly coordinating P=O oxygen donor centers and one labile chloride donor site. In this paper we describe the syntheses and the reactivity of such a ligand with an O,O,Cl donor set (Figure 1), namely $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^-$ (hereafter abbreviated as L^-).⁵

Results and Discussion

Syntheses of the Ligand. Trimethyl phosphite in chloroform splits as expected the chloride-bridged dimeric complex $[(C_6Me_6)RuCl_2]_2$ to give the mononuclear complex $[(C_6Me_6)RuCl_2\{P(OCH_3)_3\}]$ (**1**) exclusively. With trimethyl phosphite in methanol the reaction proceeds further to yield the ionic compound $[(C_6Me_6)RuCl\{P(OCH_3)_3\}_2]^+Cl^-$ (**2**). This chloride salt readily undergoes a Michaelis-Arbuzov reaction. It eliminates chloromethane to leave the neutral complex $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}\{P(OCH_3)_3\}]$ (**3**) as an orange oil when one tries to isolate **2** by boiling off the solvent. The same reaction takes place already at room temperature when **2** is dissolved in chloroform or acetone. Obviously, compound **2** is stable in solution at room temperature only when a solvent is used that effectively reduces the nucleophilicity of the chloride ion. The organometallic cation can be precipitated in an analytically pure form from methanol as the hexafluorophosphate salt $[(C_6Me_6)RuCl\{P(OCH_3)_3\}_2]^+PF_6^-$ (**4**). Upon addition of sodium iodide to a solution of **4** in acetone, both trimethyl phosphite ligands react to give CH_3I and the desired potential O,O,Cl ligand $Na[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]$ (NaL , **5**).⁶ In an attempt to purify the sodium salt **5**, it was dissolved

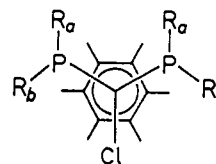


Figure 2. Newman projection of $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^-$ (L^-) along the ring-ruthenium axis, showing the two pairs of nonisochronous OCH_3 groups R_a and R_b , respectively.

in chloroform and separated from insoluble $NaPF_6$ and excess NaI . The elemental analyses and the IR and ^{31}P NMR spectra of **5** however showed that the compound still contains about 0.7 mol of $NaPF_6$. It was not possible to remove the excess $NaPF_6$ by recrystallization from dichloromethane or dichloromethane/pentane.

An alternative synthesis that we thought would avoid the presence of excess $NaPF_6$ is the Michaelis-Arbuzov reaction of the neutral compound $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}\{P(OCH_3)_3\}]$ (**3**) with sodium iodide. This did give the desired product $Na[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]$ (**5**), but again it was impure. Compound **5** prepared this way contained ca. 0.8 mol of NaI . It was not possible to remove this excess of NaI by dissolving **5** in dichloromethane and filtering off insoluble NaI . So far, we have not been able to prepare a sample of **5** that was free of additional sodium salts. We do not know yet whether this is an inherent property of **5**, but in this context it is worth mentioning that the oxygen tripod ligand $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$, which has a similar structure, can be used as an effective ionophore for the transport of alkali-metal ions through membranes.⁷ Possibly compound **5** is an efficient carrier for alkali-metal salts in nonpolar solvents too.

There have been several reports in the literature that $P(O)R_2$ ligands coordinated to metals are prone to protonation.⁸ We have observed that both Michaelis-Arbuzov products, **3** and **5**, are soluble in dilute hydrochloric acid. The protonated form of **3** can be precipitated with $NaPF_6$ at pH 1-2 to yield $[(C_6Me_6)RuCl\{P(OH)(OCH_3)_2\}\{P(OCH_3)_3\}]PF_6$ (**8**). Compound **5** (containing $NaPF_6$) gives a precipitate of $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}\{P(OH)(OCH_3)_2\}]$ (HL, **6**) at pH 3-4 in low yield (up to 40%). More of the anion $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^-$ (L^-) is precipitated at pH 1-2. Recrystallization from dichloromethane/hexane gives yellow hexagonal plates that analyze as $L_2H_3PF_6$ (**7**). The anion L^- can be handled in aqueous solutions for some time, but it slowly decomposes over a period of several days to give a mixture of yellow products that are insoluble in water. The precipitate that we have not completely characterized seems to contain hydrolysis products together with some HL.

We have found that compound **6** (HL) can be synthesized directly in high yield in a slow reaction from $[(C_6Me_6)RuCl_2]_2$ and dimethyl phosphonate, $HP(O)(OCH_3)_2$, in boiling methanol. The substitution of a chloride ligand by a $P(O)(OCH_3)_2^-$ unit with the elimination of HCl is not a common reaction in ruthenium chemistry but is well-known with $Pt(II)$.⁹ The ruthenium complexes $[\{P(OCH_3)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{(Ph_2PO)_3\}H_2]$, $[(Me_2PS_2)Ru\{(Ph_2PO)_3\}H_2]$, and $[\{RuCl_2(NO)[R(C_2H_5O)PO_2]_2\}_2]$ are the other known examples of complexes containing a $RuPOHOP$ moiety.¹⁰ They have been prepared by other methods, and only very little is known about their ability to function as ligands.

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- (6) There are several reports on Michaelis-Arbuzov reactions at coordinated trimethyl phosphite ligands. We noticed, for example, that this reaction can take place three times within the same molecule, i.e. $[(C_5H_5)Co\{P(OCH_3)_3\}_3]^{2+}$, to give $[(C_5H_5)Co\{P(O)(OCH_3)_2\}_3]^-$. See: Kläui, W.; Otto, H.; Eberspach, W.; Buchholz, E. *Chem. Ber.* **1982**, *115*, 1922. For a discussion of Michaelis-Arbuzov type reactions in transition-metal complexes, see: Brill, T. B.; Landon, S. *J. Chem. Rev.* **1984**, *84*, 577.

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Table I. ^1H NMR Spectra (Chemical Shifts (δ) and Coupling Constants (J/Hz)) of Compounds 1–9 and of the O,O,Cl Ligand L^- in Its Metal Complexes^a

compd	$\text{C}_6(\text{CH}_3)_6$ δ [$^4J(\text{PRuCCH})$]	$\text{P}(\text{O})(\text{OCH}_3)_2$ and $\text{P}(\text{OH})(\text{OCH}_3)_2$ δ [$^3J(\text{POCH})$]	$\text{P}(\text{OCH}_3)_3$ δ [$^3J(\text{POCH})$]
$[(\text{C}_6\text{Me}_6)\text{RuCl}_2\{\text{P}(\text{OCH}_3)_3\}]$ (1) ^b	2.01 d [1.3]		3.71 d [10.7]
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{OCH}_3)_3\}_2]^+\text{Cl}^-$ (2) ^c	2.14 t [1.2]		3.86 vt [11.0]
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}\{\text{P}(\text{OCH}_3)_3\}]$ (3)	2.07 t [1.0]	3.61 d [10.9] 3.62 d [10.6]	3.70 d [11.3]
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{OCH}_3)_3\}_2]^+\text{PF}_6^-$ (4)	2.11 t [1.2]		3.83 vt [11.0]
$\text{Na}[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2]$ (NaL, 5)	2.01 t [0.8]	3.55 vt [10.7] 3.57 vt [10.8]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}\{\text{P}(\text{OH})(\text{OCH}_3)_2\}]$ (HL, 6) ^d	2.11 t [0.9]	3.59 vt [11.1] 3.72 vt [10.4]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}\{\text{P}(\text{OH})(\text{OCH}_3)_2\}]$ (HL, 6) ^e	1.84 t [0.9]	3.51 vt [11.1] 3.81 vt [10.3]	
$\text{L}_2\text{H}_3\text{PF}_6$ (7) ^f	2.12 t [1.1]	3.66 vt [11.4] 3.72 vt [10.9]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{OH})(\text{OCH}_3)_2\}\{\text{P}(\text{OCH}_3)_3\}]\text{PF}_6$ (8) ^g	2.15 t [1.2]	3.77 m [11.6] 3.78 m [11.0]	3.85 m [11.1]
$[(\text{C}_6\text{Me}_6)\text{RuCl}_2\{\text{P}(\text{OH})(\text{OCH}_3)_2\}]$ (9) ^h	2.08 d [1.3]	3.76 d [10.8]	
$\{[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\}_2\text{Mg}\}$ (MgL_2)	2.06 t	3.51 vt [11.0] 3.60 vt [10.5]	
$\{[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\}_2\text{Zn}\}$ (ZnL_2)	2.07 t [0.9]	3.54 vt [11.0] 3.60 vt [10.5]	
$\{[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\}_2\text{Cd}\}$ (CdL_2)	2.05 t [0.8]	3.55 vt [10.8] 3.61 vt [10.4]	
$\{[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\}_2\text{Pb}\}$ (PbL_2)	2.05 t [0.8]	3.56 vt [10.7] 3.56 vt [10.7]	
$\{[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\}_2\text{Al}\}\text{PF}_6$ ($[\text{AlL}_2]\text{PF}_6$)	2.08 t [1.0]	3.61 vt [11.4] 3.65 vt [10.6]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Ru}(\text{C}_6\text{Me}_6)]\text{PF}_6$ ($[\text{LRu}(\text{C}_6\text{Me}_6)]\text{PF}_6$)	2.03 t [0.9]	3.50 vt [11.0] 3.53 vt [10.9]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Rh}(\text{C}_5\text{Me}_5)]\text{PF}_6$ ($[\text{LRh}(\text{C}_5\text{Me}_5)]\text{PF}_6$)	2.05 t [0.9]	3.54 vt [10.9] 3.54 vt [10.9]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Ru}(p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2)]\text{PF}_6$ ($[\text{LRu}(p\text{-cymene})]\text{PF}_6$)	2.04 t [1.0]	3.54 vt [11.0] 3.57 vt [10.9]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Re}(\text{CO})_3]$ ($\text{LRe}(\text{CO})_3$)	2.10 t [0.9]	3.59 vt [10.8] 3.60 vt [11.1]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Mo}(\text{CO})_3\text{H}]$ ($\text{LMo}(\text{CO})_3\text{H}$) ⁱ	2.07 t [0.9]	3.56 vt [10.7] 3.59 vt [11.0]	
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{W}(\text{CO})_3\text{H}]$ ($\text{LW}(\text{CO})_3\text{H}$) ⁱ	2.09 t [0.8]	3.56 vt [10.8] 3.60 vt [10.9]	

^a Measured in CDCl_3 at 80 MHz unless otherwise stated; vt is the abbreviation for virtual triplet. ^b Measured in CD_3COCD_3 . ^c Measured in CD_3OD . ^d $\delta(\text{POH})$ 12.7 (s, broad). ^e Measured in C_6D_6 ; $\delta(\text{POH})$ 12.7 (s). ^f $\delta(\text{POH})$ 10.1 (s, broad). ^g $\delta(\text{POH})$ 5.8 (s, very broad). ^h $\delta(\text{POH})$ 7.3 (s, broad). ⁱ Measured in CD_2Cl_2 .

The reaction sequence leading to compounds 1–9 and the proposed structures are summarized in Scheme I.

Spectroscopic Results. The ^1H NMR data of compounds 1–9 and of the O,O,Cl ligand L^- in its metal complexes are summarized in Table I. The 18 protons of the hexamethylbenzene ring give rise to a doublet or triplet at ca. 2 ppm depending on whether one or two phosphorus ligands are coordinated to ruthenium. The position of the signal is nearly independent of the charge of the complex, and the coupling constants $^4J(\text{PRuCCH})$ to both $\text{P}(\text{OCH}_3)_3$ and $\text{P}(\text{O})(\text{OCH}_3)_2$ are practically the same. The proton signals of the $\text{P}(\text{OCH}_3)_3$ and $\text{P}(\text{O})(\text{OCH}_3)_2$ ligands occur in the range 3.5–3.8 ppm with the $\text{P}(\text{OCH}_3)_3$ signal on the low-field side. A characteristic feature of the ^1H NMR spectra is the occurrence of “virtual” coupling in the OCH_3 region due to $^2J(\text{PRuP})$ coupling. First-order spectra (i.e. doublets with $^3J(\text{POCH}) = 10\text{--}11$ Hz) are observed only when the chemical shift difference between the two phosphorus nuclei is large compared to $^2J(\text{PRuP})$ (e.g. in the spectrum of $[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}\{\text{P}(\text{OCH}_3)_3\}]$ (3)). A complicated multiplet pattern is observed when the chemical shift difference is on the order of $^2J(\text{PRuP})$ (e.g. in the spectrum of $[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{OH})(\text{OCH}_3)_2\}\{\text{P}(\text{OCH}_3)_3\}]\text{PF}_6$ (8)¹¹), but when the shift difference is zero, the OCH_3 signals appear as “virtual” triplets.¹² There are two pairs of nonisochronous OCH_3

groups in L^- (see Figure 2), each giving rise to a “virtual” triplet. The two triplets have slightly different $^3J(\text{POCH})$ values, and the overlap of the triplets varies from 0 to 0.3 ppm depending on the actual compound. From the data for 6 (HL) in Table I, one can see that the shift difference between the triplets depends also on the solvent. The POH protons occur as broad singlets, which are sometimes difficult to observe. Probably because of fast proton-transfer reactions, their positions and half-widths are very sensitive to the kind of solvent and to traces of protic impurities in the solvent. In no case has a $^2J(\text{POCH})$ coupling been observed.

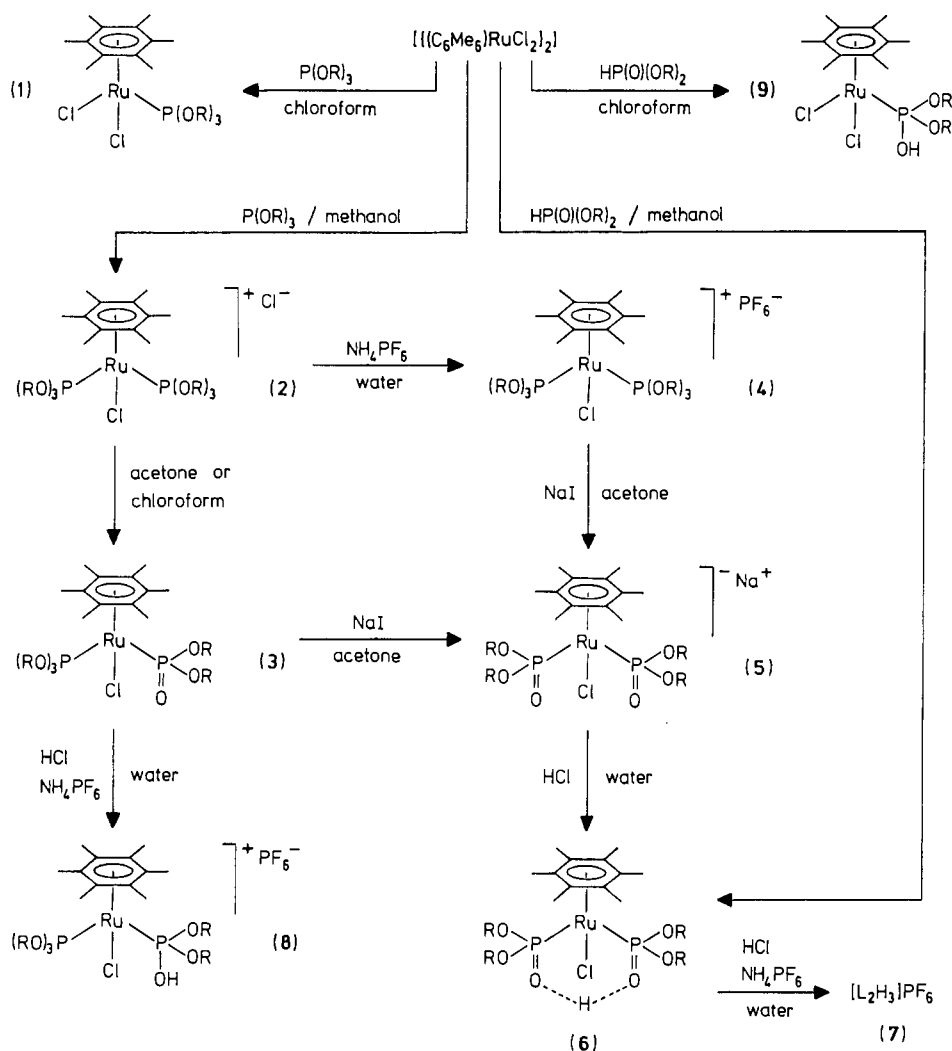
The IR spectra, recorded in the range $4000\text{--}400\text{ cm}^{-1}$, of NaL (5), HL (6), and the metal complexes of the ligand L^- (see next paragraph) show surprisingly few absorption bands considering the large number of atoms, and only the $\text{P}=\text{O}$ stretching vibration is of diagnostic value. The C—H stretching and deformation vibrations and the absorption bands at $1010\text{--}1040\text{ cm}^{-1}$, characteristic of the P—O—C unit,¹³ show no important variations of the frequency within the series of compounds described in this paper and need not be discussed here.¹⁴ The $\nu(\text{P}=\text{O})$ absorption is of high intensity and can easily be identified. This band occurs at 1260 cm^{-1} in the spectrum of $\text{HP}(\text{O})(\text{OCH}_3)_2$, but it is shifted significantly to lower frequencies upon coordination. In the

(11) The multiplet observed in the 80-MHz spectrum collapses to a simple doublet as expected when the spectrometer frequency is increased to 270 MHz.
(12) For a more detailed discussion, see: Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

(13) Thomas, L. C. *Interpretation of the Infrared Spectra of Organophosphorus Compounds*; Heyden: London, 1974.

(14) Dehnicke has discussed in more detail the IR spectra of compounds containing the related O,O,O chelating ligand $[(\text{C}_2\text{H}_5)_3\text{CoP}(\text{O})(\text{OC}_2\text{H}_5)_3]$: Kläui, W.; Dehnicke, K. *Chem. Ber.* **1978**, *111*, 451.

Scheme I. Reaction Sequence for the Preparation of Compounds 1-9, $L^- = [(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^-$ and $R = CH_3$



spectrum of NaL (5) we find this band at 1115 cm^{-1} , and in the IR spectra of the metal complexes ML_2 , $M^{2+} = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+} , it is shifted to $1095\text{--}1085\text{ cm}^{-1}$. In the ruthenium(II) compound $[(\text{hexamethylbenzene})RuL]PF_6$, where the ligand L^- experiences a higher charge density, it occurs at 1060 cm^{-1} . In the spectra of $[FeL_2]PF_6$ and HL (6) this band is around 1020 cm^{-1} , the region where we find the absorptions of the $P(O-CH_3)_2$ unit. This corresponds to a continuous decrease of the $P=O$ bond order from 2 to about 1 along this series of compounds.

Coordination Chemistry of the O,O,Cl Ligand L^- . The sodium salt NaL (5) reacts with many transition-metal and main-group-metal ions, e.g. $M^{2+} = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$ and Pb^{2+} , in water or water/methanol mixtures to give yellow precipitates. These products all have the composition ML_2 . Analogous complexes ML_2^+ form with trivalent metal ions, e.g. Al^{3+} and Fe^{3+} . They can be precipitated alternatively from HL and metal acetate salts. All ML_2 and $[ML_2]PF_6$ compounds are soluble in chloroform and dichloromethane. The 1H NMR spectra of the diamagnetic 2:1 complexes ML_2 , $M = Zn, Cd, Pb$, and Mg , show the same pattern as the spectra of NaL and HL . This means either that the compounds have the highest possible symmetry (C_{2v}), i.e. coordination number 6 with a trans arrangement of the chloride ligands, or that they are fluxional molecules. In an octahedral complex with the two chloride ligands in cis positions and in a tetrahedral complex one can expect four pairs of non-synchronous OCH_3 groups.

The geometry of the copper(II) complex CuL_2 is very probably six-coordinate with a trans arrangement of the chloride ligands. We conclude this from the similarity of its ligand-field spectrum to those of $\{[(C_5H_5)Co\{P(O)(OCH_3)_2\}_2]_2Cu\}^{15}$ and other com-

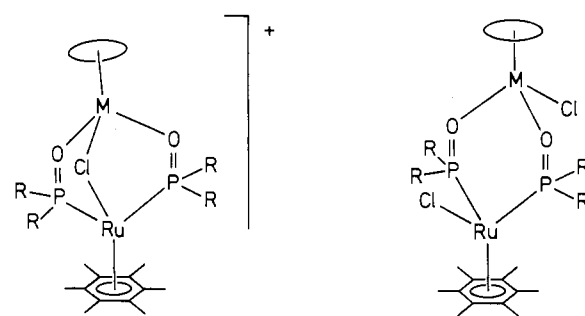


Figure 3. Possible structures of the products $[(\text{ring})MClL]$ and $[(\text{ring})ML]^+$ from the reactions of $\{[(\text{ring})MCl_2]_2\}$, $(\text{ring})M = (C_5Me_5)Rh$, and $(C_6Me_6)Ru$, with L^- as a bidentate or tridentate ligand.

parable copper(II) complexes.¹⁶ Preliminary data indicate that the cobalt complex CoL_2 is also six-coordinate and that a tetrahedral compound of the composition $LCuCl$ can be prepared.

We were interested to see whether the chelating ligand L^- can not only form 2:1 complexes with metal ions M_{aq}^{n+} but, e.g., replace halide ligands in organometallic compounds like $\{[(\text{ring})MCl_2]_2\}$, $(\text{ring})M = (C_5Me_5)Rh$ and $(C_6Me_6)Ru$. Since L^- is potentially bidentate or tridentate, the reaction of NaL with

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Table II. $\nu(\text{CO})$ Frequencies (cm^{-1}) of *fac*- $\text{Re}(\text{CO})_3$ Complexes Containing Chloride and Anionic Oxygen Ligands

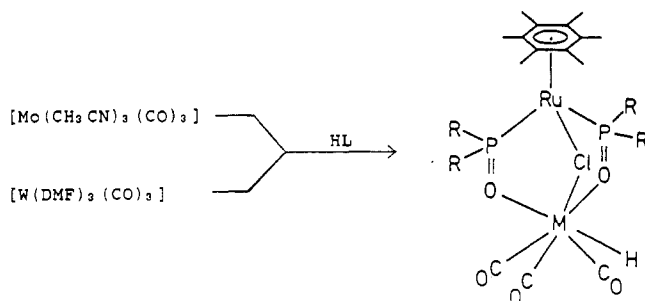
$[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2\text{Re}(\text{CO})_3]$ ($\text{LRe}(\text{CO})_3$)	2010, 1880 ^a
$[(\text{C}_5\text{H}_5)\text{Co}\{\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2\}_2\text{Re}(\text{CO})_3]$	2015, 1878 ^b
$[\text{N}(\text{C}_4\text{H}_9)_4]_2[(\text{P}_3\text{O}_9)\text{Re}(\text{CO})_3]$	2018, 1885 ^c
$[\text{N}(\text{C}_2\text{H}_5)_4]_2[(\text{CO})_3\text{ReCl}(\mu\text{-Cl})_2\text{ClRe}(\text{CO})_3]$	2025, 1900 sh, 1875 ^d
$[(\text{OH})\text{Re}(\text{CO})_3]_4$	2021, 1919 ^e

^a KBr; this work. ^b KBr; ref 29. ^c CH_3CN ; ref 30. ^d Fluorolube; ref 31. ^e THF; ref 32.

these compounds could give complexes of the composition [(ring)MCIL] or [(ring)ML]⁺ (see Figure 3). It can be assumed that these ring metal fragments require three more 2-electron ligands, as they have a strong tendency to obey the 18-electron rule. We isolated cationic complexes only; i.e., L⁻ exclusively reacted as a tridentate O,O,Cl ligand.

Ligand L⁻ reacts with $\text{ReBr}(\text{CO})_5$ in a tridentate manner, as well. In a slow reaction the bromide ligand and two carbon monoxide ligands are replaced. $\text{LRe}(\text{CO})_3$ forms yellow crystals that are soluble in most organic solvents. It decomposes in air only at temperatures above 200 °C. It is interesting to note that in the IR spectrum of $\text{LRe}(\text{CO})_3$ only two CO stretching frequencies at 2010 and 1880 cm^{-1} (KBr) are observed. At first we expected a splitting of the E band because of the nonequivalence of the oxygen and chlorine donor centers. The IR data of comparable *fac*- $\text{Re}(\text{CO})_3$ complexes (see Table II) indicate however that the two donor centers exhibit very similar electronic properties toward the rhenium tricarbonyl fragment.

Low-valent molybdenum and tungsten carbonyl derivatives are also stabilized by L⁻. Surprisingly, we found that the protonated form of the ligand, HL, smoothly reacts with $[\text{Mo}(\text{CH}_3\text{CN})_3(\text{CO})_3]$ and $[\text{W}(\text{DMF})_3(\text{CO})_3]$ at room temperature to give the metal hydride complexes $[\text{LM}(\text{CO})_3\text{H}]$.

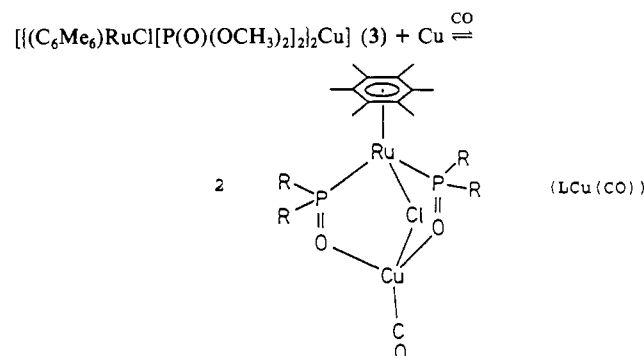


This oxidative addition reaction is reminiscent of the reaction of cyclopentadiene with metal(0) carbonyls to yield cyclopentadienylmetal hydride compounds. We know however of no example of the oxidative addition of the protonated form of a hard "classical" ligand to give molybdenum or tungsten carbonyl hydride complexes. The reaction is complete within a few minutes. In the ¹H NMR spectra of the compounds $[\text{LM}(\text{CO})_3\text{H}]$, a resonance at -4.4 (M = Mo) and -3.4 ppm (M = W) warrants the formulation as metal hydride complexes. In the ¹H NMR spectrum of $[\text{LW}(\text{CO})_3\text{H}]$ we observe a tungsten-hydride coupling constant ¹J(WH) = 10.4 Hz. The compounds are air sensitive but stable in the solid state and in dichloromethane solution under an atmosphere of dry nitrogen for several days. The molybdenum hydride is labile and rapidly gives $\text{Mo}(\text{CO})_6$ and HL when CO gas is bubbled through the solution. The tungsten hydride is unreactive under the same conditions. Preliminary experiments have shown that both metal hydride complexes can be deprotonated with potassium hydride in the presence of excess bis-(triphenylphosphine)nitrogen(1+) chloride ([PPN]Cl) to give [PPN][LM(CO)₃].

There are several examples of compounds known where hard nitrogen, oxygen, or chloride ligands are coordinated to the $\text{M}(\text{CO})_3$ unit. The complexes $[\text{LM}(\text{CO})_3\text{H}]$ are however rather rare examples of compounds where the $\text{M}(\text{CO})_3\text{H}^+$ fragment is stabilized by such ligands. Apart from the similar complexes

$[(\text{C}_5\text{H}_5)\text{Co}\{\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2\}_2\text{M}(\text{CO})_3\text{H}]$, which we have described recently,¹⁷ we are aware only of the complexes [(triazacyclononane)M(CO)₃H]⁺¹⁸ and adducts of the tetrameric species $[\{(\text{HO})\text{M}(\text{CO})_3\text{H}\}_4]$, M = Mo and W.¹⁹

In the course of a study of the coordination chemistry of copper(I) compounds, we observed that the bis(ligand)copper(II) complex CuL_2 reacts with copper metal in methanol under an atmosphere of carbon monoxide to give the copper carbonyl complex $\text{LCu}(\text{CO})$.⁵ The comproportionation reaction



takes only a few hours, and the equilibrium lies completely on the right-hand side at room temperature and 1 atm of CO gas. $\text{LCu}(\text{CO})$ can be looked at as a compound of the type $\text{Cu}(\text{CO})\text{Cl}(2\text{-electron ligand})_2$. To our knowledge $\text{LCu}(\text{CO})$ is the first neutral complex with a $\text{Cu}(\text{CO})\text{Cl}$ unit that could be isolated.²⁰ Its stability is surprising in view of the fact that neutral complexes of the type $\text{Cu}(\text{CO})\text{Cl}(\text{solvent})_2$ exist only in solutions of $\text{Cu}(\text{CO})\text{Cl}$ in, e.g., methanol or THF. They decompose upon isolation even under an atmosphere of nitrogen or carbon monoxide gas at 0 °C.²¹

Concluding Remarks

In this paper we describe a convenient synthesis of the protonated form of $[(\text{C}_6\text{Me}_6)\text{RuCl}\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2]^-$, an anion that can act potentially as a bidentate or tridentate ligand. The examples of its classical and organometallic coordination chemistry that are reported here formally look very much like the ones of the structurally analogous oxygen tripod ligands $[(\text{C}_5\text{H}_5)\text{Co}\{\text{P}(\text{O})\text{R}_2\}_3]^-$. Our preliminary experiments indicate however that they are more reactive and in this respect more interesting. We hope that we can use this O,O,Cl ligand as a dangling ligand to stabilize intermediate unsaturated organometallic fragments in catalytic reaction cycles.

Whether the anion $[(\text{C}_6\text{Me}_6)\text{RuCl}_2\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2]^-$ can act as an equally interesting O,Cl,Cl ligand in organometallic coordination chemistry remains to be seen. $[(\text{C}_6\text{Me}_6)\text{RuCl}_2\{\text{P}(\text{O})(\text{OCH}_3)_2\}_2]^-$ (**9**), the protonated form of this potential ligand, is readily accessible.

Experimental Section

All compounds are stable in air unless otherwise stated. The ¹H NMR signals of compounds 1-9 and of the O,O,Cl ligand L⁻ in the metal complexes described below are listed in Table I.

Infrared spectra were recorded on a Perkin-Elmer PE 580 spectrometer. The CO stretching frequencies were measured by using the rotational lines of dilute gaseous deuterium chloride and deuterium bromide for calibration.²² The frequencies reported below are estimated to be

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- (19) Sartorelli, U.; Garlaschelli, L.; Ciani, G.; Bonora, G. *Inorg. Chim. Acta* **1971**, *5*, 191.
- (20) Floriani et al. have prepared a comparable copper(I) iodide complex $\text{Cu}(\text{CO})\text{I}(\text{BEN})$, BEN = $\text{PhCH}=\text{NCH}_2\text{CH}_2\text{N}=\text{CHPh}$: Toth, A.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Gaetani-Manfredotti, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 648.
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accurate to ± 1 cm⁻¹. ¹H, ¹³C, and ³¹P NMR spectra were obtained on Bruker WP 80 (80 MHz) and Bruker WH 270 (270 MHz) instruments at room temperature. Chemical shifts are given in ppm (positive downfield) relative to Me₄Si and external H₃PO₄, respectively. Electron impact (70 eV) mass spectra were run on a Varian MAT CH 7 spectrometer. The elemental analyses were obtained from Analytical Laboratories, D-5250 Engelskirchen, FRG. The complexes [ReBr(CO)₃]₂²³ [Mo(CH₃CN)₃(CO)₃]₂²⁴ [W(DMF)₃(CO)₃]₂²⁵ [(C₅Me₅)RhCl₂]₂²⁶ [(C₆Me₆)RuCl₂]₂²⁷ [(p-cymene)RuCl₂]₂²⁸ and LCu(CO)₅²⁹ were prepared according to the published procedures.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₃] (1). A suspension of 55.1 mg (0.824 mmol) of [(C₆Me₆)RuCl₂] in 10 mL of chloroform was stirred with 1.0 mL of P(O)(OCH₃)₃ for 24 h. The resulting dark red solution was filtered and evaporated to dryness. The solid residue was dried under high vacuum to yield 67.3 mg (89%) of dark red crystals. The compound was recrystallized from chloroform/benzene. It is soluble in chloroform and insoluble in water, benzene, and saturated hydrocarbon solvents.

Anal. Calcd for C₁₅H₂₇Cl₂O₃PRu (M_r = 458.3): C, 39.31; H, 5.94. Found: C, 39.17; H, 5.98.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₃]⁺Cl⁻ (2). The compound was prepared from [(C₆Me₆)RuCl₂]₂ and P(O)(OCH₃)₃ in methanol as described below for compound 4. No NH₄PF₆ was added, but the solvent was removed at or below room temperature. The resulting yellow solid is stable at room temperature for some time. When the compound is heated or dissolved in acetone or chloroform, conversion to compound 3 occurs.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₃][P(O)(OCH₃)₂] (3). A suspension of 3.63 g (5.43 mmol) of [(C₆Me₆)RuCl₂] in ca. 300 mL of methanol and 5 mL of P(O)(OCH₃)₃ was stirred for 17 h, yielding a clear yellow solution. The solvent was distilled off, and the orange sticky residue was dried under high vacuum for 2 days. A 150-mL volume of chloroform was added, and the solution was set aside until the Arbuzov reaction was complete (ca. 12–48 h). The solvent was then carefully removed. The oily product crystallized completely after several hours upon addition of a few milliliters of pentane. The yield was 4.87 g (84%). The compound is soluble in water, methanol, acetone, dichloromethane, and chloroform and slightly soluble in pentane.

³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ 86.3 (d, ²J(PRuP) = 119 Hz, P(O)(OCH₃)₂), 131.9 (d, ²J(PRuP) = 119 Hz, P(O)(OCH₃)₃).

Anal. Calcd for C₁₇H₃₃ClO₆P₂Ru (M_r = 531.9): C, 38.39; H, 6.25; Cl, 6.67. Found: C, 38.24; H, 6.16; Cl, 6.80.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₃][PF₆⁻] (4). A suspension of 2.99 g (4.47 mmol) of [(C₆Me₆)RuCl₂] in ca. 300 mL of methanol and 5 mL of P(O)(OCH₃)₃ was stirred overnight, yielding a clear yellow solution. Slow addition of a solution of 1.5 g of NH₄PF₆ in 800 mL of water gave a yellow precipitate. The solution was concentrated to ca. 500 mL and filtered. The product was washed with water and dried under high vacuum. The yield was 5.50 g (89%) of fine yellow crystals. The product is soluble in methanol, acetone, chloroform, and dichloromethane, very slightly soluble in water, and insoluble in ether.

³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ -147 (sept, PF₆), 121.4 (s, P(O)(OCH₃)₃).

Anal. Calcd for C₁₈H₃₆ClF₆O₆P₃Ru (M_r = 691.9): C, 31.25; H, 5.24. Found: C, 31.54; H, 5.13.

Na[(C₆Me₆)RuCl₂][P(O)(OCH₃)₂]₂ (NaL, 5). Preparation from 4. A solution of 1.76 g (2.54 mmol) of 4 and 3.5 g of NaI in 40 mL of acetone was prepared. After 6 days the solvent was removed. The residue was dried under high vacuum and then extracted with 20 mL of dichloromethane to separate the product from insoluble salts. After filtration the clear yellow solution was evaporated to dryness and the amorphous product, which contains ca. 0.7 mol of NaPF₆, dried under high vacuum. The yield was 1.71 g.

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³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ -146 (sept, PF₆), 103.0 (s, P(O)(OCH₃)₂).

Anal. Calcd for 5 (C₁₆H₃₀ClNaO₆P₂Ru, M_r = 539.9): C, 35.60; H, 5.60. Calcd for 5-NaPF₆ (C₁₆H₃₀ClF₆NaO₆P₃Ru, M_r = 707.8): C, 27.15; H, 4.27. Found: C, 29.62; H, 4.90.

Preparation from 3. A solution of 2.50 g (4.69 mmol) of 3 in 70 mL of acetone was filtered and stirred with 4.0 g of NaI until the latter had dissolved completely. The yellow, slightly turbid solution was set aside for 2 days and then evaporated to dryness. The solid residue was extracted with ca. 50 mL of dichloromethane to separate the excess NaI. The solution was filtered and the solvent removed, giving 2.92 g of 5 in the form of a yellow amorphous solid that contained ca. 0.8 mol of NaI.

Anal. Calcd for 5 (C₁₆H₃₀ClNaO₆P₂Ru, M_r = 539.9): C, 35.60; H, 5.60. Calcd for 5-NaI (C₁₆H₃₀ClI Na₂O₆P₂Ru, M_r = 689.8): C, 27.86; H, 4.38. Found: C, 29.66; H, 4.74.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₂][P(OH)(OCH₃)₂] (HL, 6). Compound 6 was prepared according to the published procedure.⁵ It is soluble in water, methanol, acetone, dichloromethane, chloroform, THF, and benzene, slightly soluble in ether, and insoluble in saturated hydrocarbon solvents.

¹H{³¹P} NMR (270 MHz, CDCl₃): δ 2.11 (s, 18 H, C₆(CH₃)₆), 3.59 (s, 6 H, OCH₃), 3.72 (s, 6 H, OCH₃).

³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ 113.2 (s).

Mass spectrum (EI, 70 eV), *m/e* (relative intensity, fragment): 518 (43, M⁺), 486 (16, M⁺ - CH₃OH), 482 (15, M⁺ - HCl), 409 (74, M⁺ - P(O)(OCH₃)₂), 299 (100, C₆(CH₃)₆RuCl⁺).

Anal. Calcd for C₁₆H₃₀ClO₆P₂Ru (M_r = 517.9): C, 37.11; H, 6.03; Cl, 6.85. Found: C, 37.03; H, 5.90; Cl, 6.70.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₃][P(OH)(OCH₃)₂][PF₆] (8). A 132.9-mg amount (0.25 mmol) of compound 3 was dissolved in 8 mL of water, and the pH value was adjusted to 1–2 by adding dilute hydrochloric acid. Upon addition of an aqueous solution of NH₄PF₆, a yellow precipitate formed, which was separated, washed carefully with small amounts of water, and dried under high vacuum. The yield was 108.9 mg (64%) of fine crystals, soluble in methanol, acetone, dichloromethane, and chloroform, very slightly soluble in water, and insoluble in saturated hydrocarbon solvents.

³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ -147 (sept, PF₆), AB spectrum with δ₁ 122.4 and δ₂ 124.2 (²J(PRuP) = 119 Hz, P(OH)(OCH₃)₂ and P(O)(OCH₃)₃).

Anal. Calcd for C₁₇H₃₄ClF₆O₆P₃Ru (M_r = 677.9): C, 30.12; H, 5.06. Found: C, 30.13; H, 5.07.

[(C₆Me₆)RuCl₂][P(OH)(OCH₃)₂] (9). A suspension of 93.5 mg (0.14 mmol) of [(C₆Me₆)RuCl₂] in 7 mL of chloroform was stirred with ca. 0.5 mL of dimethyl phosphonate, HP(O)(OCH₃)₂, for a few hours. The resulting clear red solution was set aside for 3 days and filtered. The solvent was removed, and the residue was dried under high vacuum. Recrystallization from chloroform/pentane gave red crystals, yield 112 mg (90%).

³¹P{¹H} NMR (32.4 MHz, CDCl₃): δ 117.1 (s).

Anal. Calcd for C₁₄H₂₅Cl₂O₃PRu (M_r = 444.3): C, 37.85; H, 5.67. Found: C, 37.94; H, 5.76.

[(C₆Me₆)RuCl₂][P(O)(OCH₃)₂]₂M (ML₂; M²⁺ = Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺). Preparation from 5 (NaL, Containing NaPF₆). To a solution of ca. 150 mg of 5 in 1 mL of methanol or methanol/water was added a solution of a stoichiometric amount of the metal salt (MgSO₄·6H₂O, MnSO₄, CoCl₂·6H₂O, Ni(CH₃COO)₂·4H₂O, CuSO₄·5H₂O, Zn(CH₃COO)₂) in 0.5 mL of water. A yellow precipitate resulted, which was separated, washed with water, and dried carefully under vacuum. The compounds ML₂ are soluble in dichloromethane and chloroform, very slightly soluble in water, and insoluble in saturated hydrocarbon solvents. Recrystallization from dichloromethane/hexane gave yellow to orange crystals. The yield was 50–75%.

Ligand-field spectrum of CuL₂: 13600 cm⁻¹ (ε 15 L/(mol·cm)) ≈ 10700 (sh, ≈10).

Anal. Calcd for C₃₂H₆₀Cl₂MgO₁₂P₄Ru₂ (M_r = 1058.1): C, 36.33; H, 5.72. Found: C, 36.34; H, 5.84. Calcd for C₃₂H₆₀Cl₂MnO₁₂P₄Ru₂ (M_r = 1088.7): C, 35.30; H, 5.56. Found: C, 35.28; H, 5.58. Calcd for C₃₂H₆₀Cl₂CoO₁₂P₄Ru₂ (M_r = 1092.7): C, 35.18; H, 5.54. Found: C, 35.05; H, 5.57. Calcd for C₃₂H₆₀Cl₂NiO₁₂P₄Ru₂ (M_r = 1092.5): C, 35.18; H, 5.54. Found: C, 35.33; H, 5.57. Calcd for C₃₂H₆₀Cl₂CuO₁₂P₄Ru₂ (M_r = 1097.3): C, 35.03; H, 5.51. Found: C, 35.02; H, 5.56. Calcd for C₃₂H₆₀Cl₂O₁₂P₄Ru₂Zn (M_r = 1099.1): C, 34.97; H, 5.50. Found: C, 34.93; H, 5.52.

Preparation from 6 (HL). A suspension of ca. 150 mg of 6 in ca. 2 mL of water was stirred with a slight excess of the metal acetate (Cd(CH₃COO)₂·2H₂O, Pb(CH₃COO)₂·3H₂O). The formation of the ML₂ complexes was complete after ca. 12–20 h. The yellow precipitate was separated, washed with water, and dried carefully under high vacuum and recrystallized as described above. The yield was 52–74%.

Anal. Calcd for $C_{32}H_{60}CdCl_2O_{12}P_4Ru_2$ ($M_r = 1146.2$): Cd, 9.81; Cl, 6.19; P, 10.81. Found: Cd, 9.94; Cl, 5.98; P, 10.64. Calcd for $C_{32}H_{60}Cl_2O_{12}P_4PbRu_2$ ($M_r = 1241.0$): C, 30.97; H, 4.87. Found: C, 30.87; H, 4.85.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2M]PF_6$ ($[ML_2]PF_6$, $M^{3+} = Al^{3+}$, Fe_3^{3+}). The compounds were prepared from **5** and $Al(NO_3)_3 \cdot 9H_2O$ or $FeCl_3 \cdot 6H_2O$ in water or water/methanol as described above. An excess of $NaPF_6$ was added to precipitate the salts completely. The yield was 60–80%. The products were recrystallized from chloroform/ether or acetone/ether to give fine black crystals of $[FeL_2]PF_6$ and yellow crystals of $[AlL_2]PF_6$.

Anal. Calcd for $C_{32}H_{60}AlCl_2F_6O_{12}P_3Ru_2$ ($M_r = 1205.7$): C, 31.88; H, 5.02. Found: C, 32.0; H, 5.26. Calcd for $C_{32}H_{60}Cl_2F_6FeO_{12}P_3Ru_2$ ($M_r = 1234.6$): C, 31.13; H, 4.82. Found: C, 31.13; H, 4.96.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Ru(C_6Me_6)]PF_6$ ($[LRu(C_6Me_6)]PF_6$). To a solution of 0.243 mmol of $Na[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]$ (**5**, NaL) in methanol/water was added a solution of 0.121 mmol of $[(C_6Me_6)RuCl_2]$ in methanol. Slow addition of a concentrated solution of NH_4PF_6 in water gave a yellow precipitate, which was separated, washed with water, and dried under high vacuum. Recrystallization from acetone/ether gave orange-red crystals, yield 210 mg (93%).

1H NMR (80 MHz, $CDCl_3$): δ 2.08 (s, 18 H, $C_6(CH_3)_6RuL$).

Anal. Calcd for $C_{28}H_{48}ClF_6O_6P_3Ru_2$ ($M_r = 925.2$): C, 36.35; H, 5.23. Found: C, 36.28; H, 5.35.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Rh(C_5Me_5)]PF_6$ ($[LRh(C_5Me_5)]PF_6$) and $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Ru(p-CH_3C_6H_4CH(CH_3)_2)]PF_6$ ($[LRu(p-cymene)]PF_6$). The compounds were prepared as described for $[LRu(C_6Me_6)]PF_6$ from $[(C_5Me_5)RhCl_2]$ and $[(p-cymene)RuCl_2]$ in 80–90% yield. $[LRh(C_5Me_5)]PF_6$ was characterized as follows.

1H NMR (80 MHz, $CDCl_3$): δ 1.62 (s, 15 H, $C_5(CH_3)_5$).

Anal. Calcd for $C_{26}H_{44}ClF_6O_6P_3RhRu$ ($M_r = 900.0$): C, 34.70; H, 5.04. Found: C, 34.64; H, 5.11.

$[LRu(p-cymene)]PF_6$ was characterized as follows.

1H NMR (80 MHz, $CDCl_3$): δ 1.34 (d, $^3J(HCCH) = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 2.23 (s, 3 H, $C_6H_4CH_3$), 2.85 (sept, $^3J(HCCH) = 6.8$ Hz, 1 H, $CH(CH_3)_2$), 5.40 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{26}H_{44}ClF_6O_6P_3Ru_2$ ($M_r = 897.1$): C, 34.81; H, 4.94. Found: C, 34.63; H, 5.14.

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Re(CO)_3]$ ($[LRe(CO)_3]$). A 79-mg amount (0.19 mmol) of $[ReBr(CO)_5]$ and 101 mg (0.19 mmol) of complex **6** (HL) in 30 mL of chloroform were heated to reflux under a nitrogen atmosphere for 24 h. The solution was concentrated and chromatographed on a short silica column. A yellow band was eluted

with chloroform/acetone (20:1). Evaporation of the solvent and recrystallization from chloroform/pentane gave 103 mg (0.13 mmol, 67%) of orange-yellow crystals. The compound $LRe(CO)_3$ is stable in air, soluble in acetone, dichloromethane, chloroform, and THF, and insoluble in saturated hydrocarbon solvents.

Anal. Calcd for $C_{19}H_{30}ClO_9P_2ReRu$ ($M_r = 787.1$): C, 28.99; H, 3.84. Found: C, 28.83; H, 3.79.

IR (CH_2Cl_2 , $\nu(CO)$): 2018 (st), 1889 (st, br) cm^{-1} .

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2Mo(CO)_3H]$ ($[LMo(CO)_3H]$). A 63-mg amount (0.21 mmol) of $[Mo(CH_3CN)_3(CO)_3]$ as added to a solution of 108 mg (0.21 mmol) of **6** in dichloromethane. The reaction mixture was stirred under nitrogen for 30 min and then filtered. Slow evaporation of the solvent gave 133 mg (92%) of large yellow to brown air-sensitive crystals.

IR (CH_2Cl_2 , $\nu(CO)$): 2007 (st), 1915 (st), 1884 (m) cm^{-1} .

1H NMR (80 MHz, CD_2Cl_2): δ -4.4 (s, Mo-H).

$[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2W(CO)_3H]$ ($[LW(CO)_3H]$). This compound was prepared in a manner analogous to that for $LMo(CO)_3H$ from 108 mg (0.21 mmol) of $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2P(OH)(OCH_3)_2]$ (HL) and 101 mg (0.21 mmol) of $[W(DMF)_3(CO)_3]$; yield 159 mg (97%) of large yellow to brown air-sensitive crystals.

IR (CH_2Cl_2 , $\nu(CO)$): 1994 (st), 1899 (st), 1872 (sh), 1845 (m) cm^{-1} .

1H NMR (80 MHz, CD_2Cl_2): δ -3.4 (t, $^3J(POWH) = 1.3$ Hz, satellites with $^1J(WH) = 10.4$ Hz, W-H).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ 16.0 (q, $^1J(CH) = 104$ Hz, CCH_3), 51.3 (q, $^1J(CH) = 146$ Hz, OCH_3), 51.7 (q, $^1J(CH) = 146$ Hz, OCH_3), 104.9 (s, CCH_3), 218.4 (d, $^2J(CWH) = 16.0$ Hz, satellites with $^1J(^{183}WC) = 154$ Hz, $C\equiv O$).

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Note Added in Proof. The perchlorate salt of $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^+$ and compound **1** have recently been prepared in a similar way: Rojas, A.; Scotti, M.; Valderrama, M. *Bol. Soc. Chil. Quim.* **1988**, *33*, 103.

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Reactions of Arenediazonium Salts with Hexacarbonyldicobalt Derivatives. Synthesis of Cationic *N*-Aryldiazadibocobaltatetrahedranes and Crystal and Molecular Structure of $[Co_2(CO)_4(\mu-Ph_2PCH_2PPh_2)(\mu-N_2C_6H_4-4-CH_3)][SbF_6]$

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$Co_2(CO)_4(\mu-CO)_2(\mu-dppm)$ ($dppm = \text{bis}(\text{diphenylphosphino})\text{methane}$) reacts with a variety of arenediazonium salts in dichloromethane at temperatures well below ambient to produce a series of novel *N*-aryldiazadibocobaltatetrahedrane cations as their $[BF_4^-]$, $[PF_6^-]$, and $[SbF_6^-]$ salts. The spectroscopic characterizations of these new compounds are discussed, and the structure of $[Co_2(CO)_4(\mu-N_2C_6H_4-4-CH_3)(\mu-dppm)][SbF_6]$ has been determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca*, with unit cell dimensions $a = 22.488$ (5) Å, $b = 19.459$ (4) Å, $c = 18.002$ (4) Å, $V = 7877$ (3) Å³, and $Z = 8$. The structure refined to $R(F) = 5.40\%$. It is an isolobal analogue of tetrahedrane; the distorted tetrahedral Co_2N_2 core contains a 1.342 (12) Å N–N bond (midway between a single and a double bond) and a Co–Co distance of 2.440 (2) Å.

Introduction

Since the first report more than 20 years ago,² reactions of arenediazonium ions with nucleophilic transition-metal compounds

have produced a profusion of neutral, monocationic, and even dicationic aryldiazanyl and aryldiazene derivatives of most of the transition metals.³ A rather small subset involves the ArN_2 moiety

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