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Cationic Osmium(II) Acetyl Complexes Bearing Pyrazolylmethane Ligands: Intramolecular and Interionic Structure and Isolation of an Intermediate Containing the "Os−I−Ag" Moiety

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The reaction of the complexes *cis,trans*-[OsI(Me)(CO)$_2$(PMe$_3$)$_2$] and *fac*-[OsI(Me)(CO)$_3$(PMe$_3$)] with silver salts (AgX) and bis- and tris(pyrazol-1-yl)methane ligands affords the complexes [Os(COMe)((pz)$_2$CH$_2$)(CO)(PMe$_3$)Y]$^+$[BPh$_4$]$^-$ (Y = PMe$_3$, CO) and [Os(COMe)((pz)$_3$CH-κ^2)(CO)(PMe$_3$)Y]$^+$[BPh$_4$]$^-$ (Y = PMe$_3$, CO) or the solvento complexes *cis,trans*-[Os(Me)(S)(CO)$_2$(PMe$_3$)$_2$]$^+$X$^-$ depending on the reaction conditions. In the reaction of *cis,trans*-[OsI(Me)(CO)$_2$(PMe$_3$)$_2$] with AgX in the presence of (pz)$_3$CH, the intermediate complexes [(Me)(CO)$_2$(PMe$_3$)$_2$Os(μ-I)Ag((pz)$_3$CH)]$^+$[X]$^-$ (X$^-$ = CF$_3$SO$_3$$^-$, BF$_4$$^-$) were isolated. The solution interionic structures of cationic complexes were investigated by ^{1}H NOESY or ^{19}F{^{1}H} HOESY NMR spectra.

Introduction

The use of reagents that create an electronic unsaturation on a metal by abstracting a halogen atom is one of the most widely used methodologies in organometallic chemistry today. Several Lewis acids can be used, ranging from the "classical" silver or thallium salts to the more recently used borane compounds.[1]

In past studies we have shown that the complexes *cis,trans*-[MI(Me)(CO)$_2$(PMe$_3$)$_2$] (where M = Fe, Ru)[2] and *fac*-[RuI(Me)(CO)$_3$(PMe$_3$)][3] undergo easy ionization of the M−I bond, especially in polar solvents such as methanol. We have taken advantage of this phenomenon as well as the strong tendency in such complexes for the Me to migrate onto a cis CO to synthesize acetyl compounds containing N,X-bidentate (X = N, O)[2,4] or N,N,N-tridentate ligands.[2,3,5] Such compounds were used as model compounds to develop a methodology for investigating the relative anion−cation position (interionic structure) in solution based on the detection of interionic NOE contacts in the ^{1}H NOESY or ^{19}F{^{1}H} HOESY NMR spectra.[6]

To complete the series of compounds which come from the reaction of *cis,trans*-[MI(Me)(CO)$_2$(PMe$_3$)$_2$] and *fac*-[MI(Me)(CO)$_3$(PMe$_3$)] with N,N- or N,N,N-ligands, we decided to investigate the reactivity of Os analogues. In comparison to the Fe and Ru complexes, the strength of the Os−I bond is strong enough to preclude "spontaneous" ionization, even in polar solvents. For this reason, Lewis acids were used to facilitate the ionization. Even with these reagents the ionization can be difficult, depending on the experimental conditions.

In this paper we report the synthesis and characterization of (1) cationic acetyl complexes **3**, **4**, **10**, and **11** containing N,N- or κ^2-N,N,N-ligands (Scheme 1), (2) cationic solvento complexes **7**−**9** that are formed by the abstraction of I$^-$ from initial substrates (Scheme 1), and (3) the intermediate compound derived from the attack of silver, whose Lewis acidity is reduced by the coordination of the tris(pyrazolyl)methane, at the Os−I bond (Scheme 2). Furthermore, the results relative to the investigation of the solution interionic structure for all the cationic compounds, except the solvento complexes, are also reported.

Results and Discussion

Synthesis. The reactions of complexes **1** and **2** with silver salts (AgX), in methanol, afford the unsaturated intermediate **I** (Scheme 1), which, in the presence of the bis- or tris(pyrazolyl)methane ligands, is transformed into the cationic acetyl complexes **3**, **4**, **10,** and **11**. The

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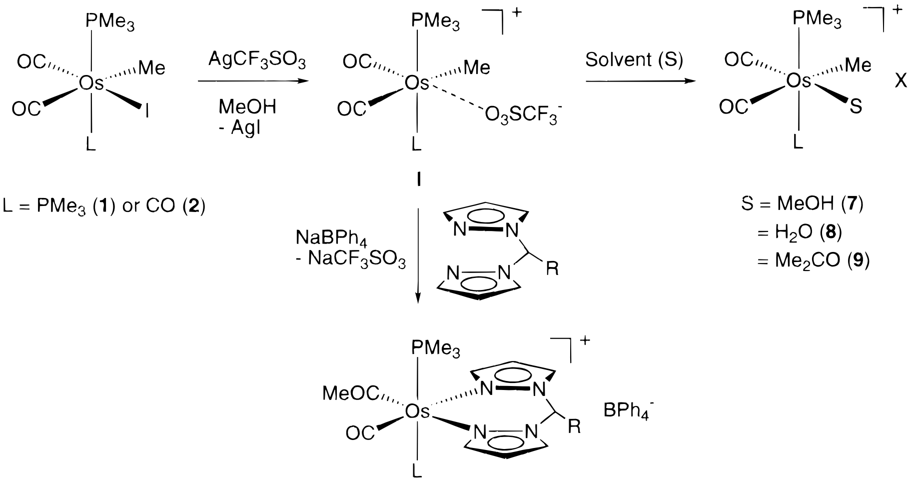
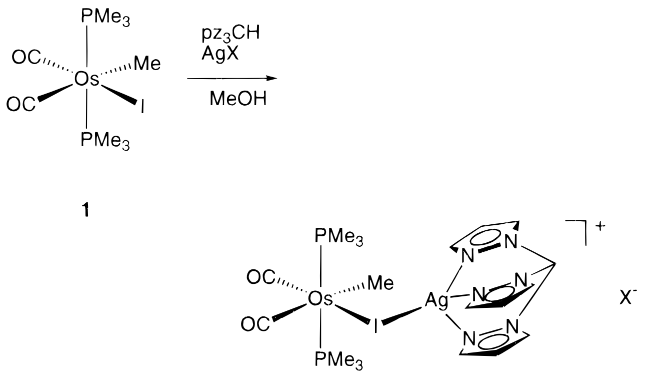
Scheme 1



L = PMe$_3$; R = H (**3**) or pz (**4**)
L = CO; R = H (**10**) or pz (**11**)

Scheme 2



X = $CF_3SO_3^-$ (**5**) or BF_4^- (**6**)

silver salts must be added to the solutions containing the complexes in the absence of the pyrazolyl ligands in order to obtain the desired products. In fact, if the reactions are carried out in the presence of the pyrazolyl ligands, they are slowed or completely inhibited. The reaction of complex **1** with the tris(pyrazolyl)methane ligand, where AgX is added to a solution which already contains the ligand, gives complexes **5** and **6** (Scheme 2). Furthermore, the reactions of complexes **1** and **2** with AgX cannot be protracted or forced by increasing the temperature because complex **7** forms, which does not react with the pyrazolyl ligands. Finally, complex **11** does not decarbonylate even with increased temperature (up to 65 °C) and bubbling N_2 in CH_2ClCH_2Cl.

The results reported and summarized in Schemes 1 and 2 confirm the considerably higher inertness of osmium complexes compared to the analogous iron and ruthenium complexes. Previous studies have shown that the complexes *cis,trans*-[MI(Me)(CO)$_2$(PMe$_3$)$_2$][2] (M = Fe, Ru) and *fac*-[RuI(Me)(CO)$_3$(PMe$_3$)][3] are good precursors for preparing cationic acetyl complexes containing bi- and tridentate ligands. This is due to (a) the possibility of easily ionizing the M−I bond, (b) the tendency of the Me group to migrate onto a cis CO and, (c) in the case of *fac*-[RuI(Me)(CO)$_3$(PMe$_3$)], the elimination of a CO group. The results reported here on the analogous osmium complexes **1** and **2** indicate that it is much more difficult to obtain all three types of reactions mentioned above. Only by treating complexes **1** and **2** with silver salts AgX is it possible to force the ionization of the Os−I bond, and the Lewis acidity of such salts must not be reduced by the presence of the nitrogen ligands that could potentially coordinate to the silver. It is known from the literature that both (pz)$_2$CH$_2$[7] and (pz)$_3$CH[8] coordinate to Ag(I). By using the tris(pyrazolyl)methane ligand we have intercepted the intermediates **5** and **6**, where the Os−I bond is weakened but still present. Once one arm of the ligands is coordinated to osmium, the migration of the Me group onto a cis CO occurs quite easily. The κ^1-coordinated complex was never observed, even by IR spectroscopy, during the course of the reactions. It is quite surprising that complex **11** does not decarbonylate, because the analogous Ru(II) complex decarbonylates easily, affording a mixture of methyl complexes.[3] According to our previous studies, the thermodynamics of such a reaction are favored in the case of osmium,[9] which suggests that complex **11** does not decarbonylate for kinetic reasons; presumably, the Os−CO bond is too strong to be broken.

Compounds **5** and **6** represent, to the best of our knowledge, the first bimetallic compounds where Os and Ag are linked together by a single halogen bridge. Interestingly, their stability is affected by the nature of the counterion. While complex **6** is stable for several days in methylene chloride solution, complex **5** slowly transforms into *trans,trans*-[Os(Me)(CF$_3$SO$_3$)(CO)$_2$(PMe$_3$)$_2$] and (pz)$_3$CH with the precipitation of AgI. Adducts similar to compounds **5** and **6** containing a silver atom bridged to two iodide atoms bonded to rhenium[10] or the single bridge Pt−Cl−Ag[11] were previously reported.

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The reaction yields that afford complexes **3**, **4**, **10**, and **11** are low for two reasons: (1) the silver salts have to be used in less than stoichiometric amount in order to avoid redox processes on osmium and (2) the ionization process does not go to completion due to the formation of the solvento and/or X^- complexes. Attempts were made to eliminate the second limitation by carrying out the reaction in non-coordinating solvents and by using less coordinating counterions, but they were unsuccessful because of the insolubility of the intermediate (in benzene and toluene) and the activation of radical processes in chlorinated solvents.

Structural Characterization. (a) Solution Intramolecular Structure. The complexes were characterized by IR and ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopy. The structures of complexes **3**, **4**, and **7**−**11** were easily determined by combining the information from IR and NMR spectroscopy. For complexes **3** and **4** the IR spectra show two bands in the carbonyl stretching region due to the COMe and CO ligands. Both ^{1}H and ^{13}C NMR spectra of complex **3** indicate the presence of deceptive triplets, typical of $X_nAA'X'_n$ systems,[12] which ensure that the two PMe_3 groups are mutually trans. ^{1}H, ^{13}C, and ^{31}P NMR spectra for complex **4** indicate that there are still two PMe_3 groups but which are not equivalent. Only one of these shows NOE contacts with the uncoordinated pyrazolyl ring and can therefore be assigned. ^{1}H and ^{13}C NMR spectra of complexes **3** and **4** show 7 and 10 resonances, respectively, due to the 2 and 3 nonequivalent pz rings and to the CH and CH_2 protons and carbons. The different rings can be distiguished by the detection of a NOE contact between the COMe and the 3-protons in cis positions and a NOE between one PMe_3 group and the 3″-proton of the uncoordinated ring. In the case of complex **4** the two phosphorus atoms are not equivalent and in the ^{31}P NMR spectrum it is possible to observe $^2J_{PP}$; its value (251.6 Hz) is between those of analogous complexes of iron (162 Hz) and ruthenium (292 Hz).[13]

The determination of the structure of complexes **10** and **11** proceeds in a similar way. The IR spectra show three bands in the carbonyl stretching region due to the COMe and CO ligands. This ensures that the two carbonyls are mutually cis. In the ^{13}C NMR spectra two resonances are present which are due to the CO groups and the coupling constants $^2J_{PP}$ have very different values (ca. 10 and ca. 90 Hz), indicating that one CO is cis and the other is trans to the PMe_3 group. The absence of a NOE contact between the PMe_3 and the pz ring protons for complex **11** indicates that the uncoordinated pz ring stays in front of the CO trans to the phosphine.

The structure of complexes **7**−**9** was easily determined in the IR spectra with the observation of two bands due to terminal carbonyls. The ^{1}H, ^{13}C, and ^{31}P NMR resonances are consistent with those predicted on the basis of the structures reported in Schemes 1 and 2.

In the ^{1}H NMR spectra of complexes **5** and **6**, in addition to the typical resonances due to the PMe_3 and Me groups, there are four resonances that can be reasonably assigned to the pyrazolyl rings. Three of them are integrated for three protons (3, 4, and 5), and one is integrated for one proton (CH). This indicates that the three pyrazolyl rings are equivalent. Interestingly, they remain equivalent with decreasing temperature (up to 217 K). The ^{13}C NMR spectrum of complex **6** confirms these indications. The fact that the pyrazolyl rings are close to the "Os moiety" is demonstrated by the clear NOE contacts between the 3-protons and PMe_3 and Me protons (Figure 1). IR spectra add another important piece of information. The CO stretching bands (2018 and 1949 cm^{-1}) fall just between those due to the cationic (ca. 2030 and 1970 cm^{-1}) and the starting neutral complexes (2010 and 1932 cm^{-1}), indicating that the Os−I bond is weakened but not broken. Considering that (a) complex **5** in methylene chloride slowly affords the precipitation of a solid that qualitative tests indicate to be AgI with the formation of a methyl complex (see below) and (b) the elemental analyses are correct, their structure must be that formulated. To our knowledge complexes **5** and **6** represent the first complexes containing the "Os−I−Ag" bridge. Unfortunately, we were unable to obtain crystals suitable for X-ray single-crystal investigation and we have no information about the structural properties of the "Os−I−Ag" bond. Attempts were made to understand whether this bond is bent or linear by quantifying the NOE between the pyrazolyl and PMe_3 or Me protons. The results were not conclusive, because it was impossible to freeze the motion that mediates the pyrazolyl ring environments.

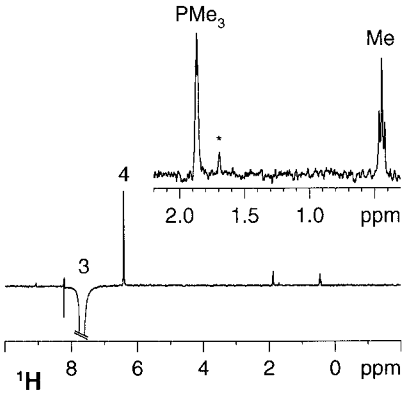

Figure 1. Selno[20] ^{1}H NMR spectrum recorded in CD_2Cl_2 for complex **6** showing the NOE contacts of the 3-protons belonging to the pz rings with the 4-protons and with PMe_3 and Me protons. An asterisk denotes a very weak NOE of the 3-proton or some other coincident proton with the PMe_3 protons of a complex that is forming slowly. By using the Selno sequence the NOE is directly shown as an NOE difference spetcrum.

As mentioned above, when complex **5** is left in methylene chloride solution, the complex *trans,trans*-[Os(Me)(CF_3SO_3)(CO)$_2$(PMe_3)$_2$] is obtained. It was characterized spectroscopically in solution. The ^{19}F NMR spectrum of its mixture with complex **5** shows two singlets at −78.4 and −79.3 ppm, which indicates that two types of $CF_3SO_3^-$ groups must be present. From the characterization of complex **5** we know that the signal at −79.3 ppm is due to the noncoordinated $CF_3SO_3^-$

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group (see below), which indicates that the other resonance is assignable to $CF_3SO_3^-$ coordinated to osmium. This is confirmed by the fluorine atoms having relevant NOE with their PMe_3 and Me protons. Cases in which free and coordinated triflate counterions show different chemical shifts have been previously reported in the literature.[14] Another indication that the $CF_3SO_3^-$ group is coordinated is that the CO stretching band value at 1950 cm^{-1} is typical of analogous neutral compounds having the two carbonyls in mutually trans positions.

(b) Solution Interionic Structure. The interionic structure of the cationic complexes **3**−**6**, **10**, and **11** was investigated in methylene chloride-d_2 by ^1H NOESY and $^{19}F\{^1H\}$ HOESY NMR spectra. The observation of interionic contacts in all the spectra confirms that such complexes are present mainly as intimate ion pairs in methylene chloride. Furthermore, the interionic structure of complexes **3** and **10** is practically identical with those of the isoelectronic compounds of iron and ruthenium for **3**[2] and ruthenium for **10**.[3] The protons of the counterion interact specifically with the 5, CH_2, and PMe_3 protons. Since no interaction is observed with the COMe protons, the counterion is localized close to the pz rings and phosphine groups due principally to electrostatic gain.

More interesting are the results from the investigation of the interionic structure of complexes **4** and **11**. The analogous ruthenium complex **4** shows a dynamic process that averages the environments of the three pyrazolyl rings and prevents obtaining detailed information about its interionic structure. The interionic structure of the analogous ruthenium complex of **11** cannot be studied because, in solution, it rapidly transforms into the κ^3-coordinated complex via a decarbonylation process. For complex **4** we observed strong interionic contacts between (a) *o*-H with 5,5′ and CH protons and (b) *o*-H, *m*-H, and *p*-H with the protons belonging to the phosphine group that does not "see" the free pz ring (PMe_3^A). The ^1H NOESY NMR spectrum of complex **11** showed the following interionic contacts: *o*-H with 5,5′ and CH protons and (b) *m*-H and *p*-H with PMe_3 protons. In both cases, only two of the 5-protons interact with the *ortho* protons of the counterion and, in particular, the 5-protons belonging to the coordinated pz rings (Figure 2). Furthermore, in the case of complex **4**, only the protons of the PMe_3 group that stay far from the free pz ring interact with the protons of the counterion. In the resulting interionic structure the counterion stays on the side of the coordinated pz rings shifted far from the noncoordinated pz ring.

The interionic structure of complex **5** is remarkable because the counterion interacts exclusively with the CH and 5-protons (see Figure 3).

(c) Molecular Structure of 8. The molecular structure of complex **8** is shown in Figure 4 with the crystallographic numbering and consists of a *cis,trans*-$[Os(Me)(H_2O)(CO)_2(PMe_3)_2]^+$ cation and a $CF_3SO_3^-$ counterion. Relevant bond distances and angles are reported in Table 1. The cation shows octahedral coordination around the Os center with the two trimethylphosphine ligands occupying trans positions (P(1)−Os−P(2) = 175.6(1)°). The two Os−P distances

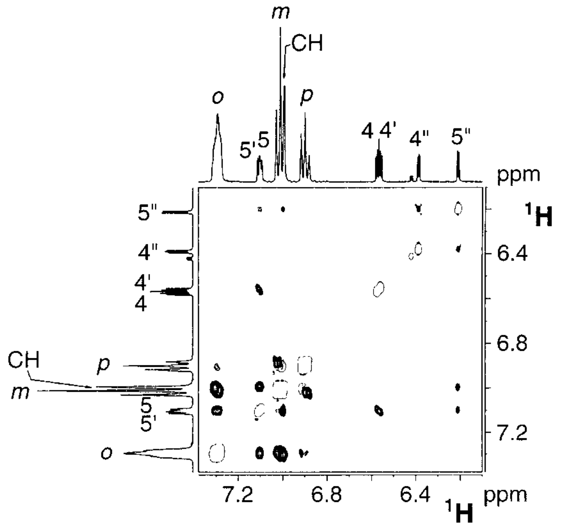

Figure 2. Section of the ^1H NOESY NMR spectrum for complex **4** showing the selective interaction of the coordinated 5-protons with *o*-H protons.

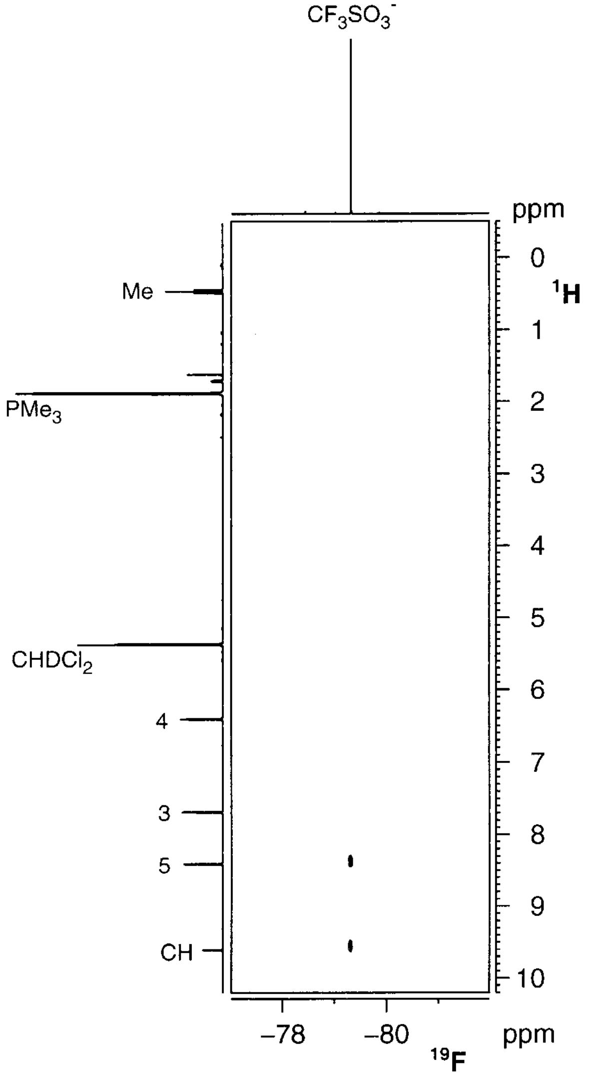

Figure 3. $^{19}F\{^1H\}$ HOESY NMR spectrum of complex **5** recorded in CD_2Cl_2 showing the specific interactions of 5-protons and CH protons with $CF_3SO_3^-$.

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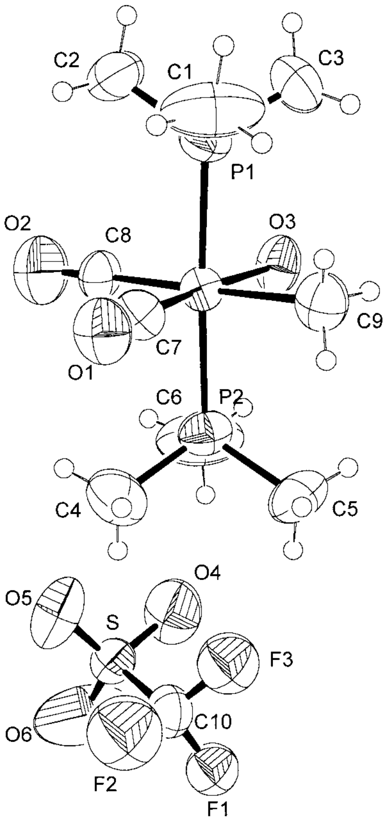

Figure 4. ORTEP drawing of the molecular structure of **8** (50% probability thermal ellipsoids).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 8[a]

Os−P1	2.368(3)	Os−C8	1.941(9)
Os−P2	2.377(3)	Os−C9	2.159(10)
Os−O3	2.155(6)	O1−C7	1.133(10)
Os−C7	1.834(9)	O2−C8	1.121(11)
P1−Os−P2	175.6(1)	P2−Os−C8	88.5(3)
C7−Os−C8	93.2(4)	P2−Os−C9	92.2(3)
C7−Os−C9	88.5(4)	P2−Os−O3	85.8(2)
C8−Os−C9	178.1(4)	P1−Os−C7	91.6(3)
O3−Os−C7	175.5(3)	P1−Os−C8	92.0(3)
O3−Os−C8	91.0(3)	P1−Os−C9	87.2(3)
O3−Os−C9	87.3(3)	P1−Os−O3	89.8(2)
P2−Os−C7	92.8(3)	Os−C7−O1	176.5(9)
		Os−C8−O2	177.0(9)
O3···O4(i)	2.64(1)	C9···O5(ii)	3.44(1)
O3···O5(ii)	2.71(1)		
C9−H9···O5	160.2(9)		

[a] Symmetry transformations: (i) $0.5 + x$, $0.5 - y$, $-0.5 + z$; (ii) $1 + x$, y, z.

(2.368(3) and 2.377(3) Å) are comparable within the limit of the experimental error. The two cis CO ligands exhibit quite different metal to carbon bond lengths (1.834(9) and 1.941(9) Å, respectively), reflecting the different trans influences of the methyl and oxygen ligands, respectively. The Os−O distance, 2.155(6) Å, is comparable with analogous distances in octahedral Os complexes with trans CO ligands.[15,16] The oxygen atom is part of a water molecule, the hydrogen atoms of which could not be located in the difference Fourier maps. It is involved in two short interionic (H-bond) interactions with two different oxygen atoms of two molecules of triflate counterions (donor−acceptor distances 2.644 and 2.708 Å; see Table 1). The Os−C$_{met}$ value, 2.16(1) Å, falls within the range of values typically found for osmium−sp^3 carbon distances.[17] The triflate counterion shows the staggered conformation which is normally seen for the free anion in the solid state.

Apart from the cation/anion interactions described above, packing is also determined by a weaker H-bond interionic interaction of the C−H···O kind (D···A distance 3.44 Å; Table 1).

Conclusions

We have shown how the reactivity of the complexes *cis,trans*-[MI(Me)(CO)$_2$(PMe$_3$)$_2$] and *fac*-[MI(Me)(CO)$_3$(PMe$_3$)] toward bis- and tris(pyrazolyl)methane ligands is slower when M = Os than when M = Fe, Ru. This is substantially due to the preliminary difficulty of ionizing the Os−I bond that necessitates the addition of silver salts. Furthermore, the Lewis acidity of silver salts must not be reduced by the coordination of the pyrazolyl ligands. As a confirmation, in the case of the reaction of *cis,trans*-[OsI(Me)(CO)$_2$(PMe$_3$)$_2$] with (pz)$_3$CH the intermediate [(Me)(CO)$_2$(PMe$_3$)$_2$Os(μ-I)Ag((pz)$_3$CH)]$^+$[X]$^-$, where two metal-containing moieties are linked together by a single halogen bridge, has been intercepted. The reaction yields are also lower due to relevant competition of the pz ligands with solvent and counterions.

The interionic structure of the complexes where the pz ligands are coordinated to osmium has been investigated in methylene chloride solution. Interestingly, in complexes containing κ^2-coordinated pz ligands, the counterion interacts specifically with protons belonging to the coordinated rings. In the complex intermediate [(Me)(CO)$_2$(PMe$_3$)$_2$Os(μ-I)Ag((pz)$_3$CH)]$^+$[X]$^-$, the counterion is localized just close to the peripheral protons of the (pz)$_3$CH ligand.

Experimental Section

Complexes **1** and **2** were prepared according to the literature.[17] Reactions were carried out in a dried apparatus under a dry inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified prior to use by conventional methods.[18] The (pz)$_2$CH$_2$ and (pz)$_3$CH ligands were synthesized according to the literature.[19] Pyrazole was purchased from Fluka and used without further purification.

IR spectra were taken on a 1725 X FTIR Perkin-Elmer spectrophotometer. One- and two-dimensional ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were measured on Bruker DPX 200 and DRX 400 NMR spectrometers. Referencing is relative to TMS (^{1}H and ^{13}C), CFCl$_3$ (^{19}F), and 85% H$_3$PO$_4$ (^{31}P). NMR samples were prepared by dissolving about 20 mg of compound in 0.5 mL of deuterated solvent. Two-dimensional ^{1}H NOESY and ^{19}F{^{1}H} HOESY spectra were recorded with a mixing time of 500−800 ms. The monodimensional NOE experiments were per-

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formed by using the Selno sequence[20] with a mixing time ranging from 50 to 450 ms.

X-ray Crystallography. Crystals of **8** suitable for X-ray single-crystal analysis were obtained from CH_2Cl_2/*n*-hexane. Diffraction intensities were collected at room temperature by the ω-scan method on a graphite-monochromated Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.710 69 Å). The unit cell parameters were determined by least-squares refinement of 25 reflections. Crystal data are as follows: $C_{10}H_{23}F_3O_6OsP_2S$, $a = 8.742(1)$ Å, $b = 23.683(5)$ Å, $c = 10.049(3)$ Å, $\beta = 106.87(2)°$, $Z = 4$, monoclinic, space group $P2_1/n$, $\mu = 6.72$ cm^{-1}. A total of 3686 reflections were collected (θ range 2.5−25°), 2568 of which were $>2\sigma(I)$. Diffraction intensities were reduced to F_o^2 values. The structure was solved by direct methods and refined by full-matrix least-squares calculations. Triflate anion was found to be affected by disorder, and two different positions for the F atoms could be located in the difference Fourier maps with similar occupation factors (0.56 for the main image). Thermal vibrations were treated anisotropically except for the fluorine atoms. H atoms were geometrically positioned (C−H = 0.96 Å) and refined "riding" on their corresponding carbon atoms. Absorption correction was applied by the Walker and Stuart method[21] once a complete structural model was obtained (including the triflate disorder), and all atoms were refined isotropically. Refinement converged at a final R1 = 0.037, wR2 = 0.088, and S = 1.055. Residual electron density peaks of about 1 e Å^{-3} were found in the proximity of the Os atom.

For all computations the SHELXTL[22] package of crystallographic programs was employed.

Synthesis of Complexes. *trans*-[Os(COMe)((pz)$_2$CH$_2$)(CO)(PMe$_3$)$_2$]$^+$[BPh$_4$]$^-$ (3). Complex **1** (50 mg, 0.093 mmol) and $(pz)_2CH_2$ (20 mg, 0.140 mmol) were dissolved in 4 mL of MeOH. Solid $Ag(CF_3SO_3)$ (21 mg, 0.08 mmol) was added to the solution. Immediately, AgI started to precipitate and after 20 min it was filtered off. When a large excess of $NaBPh_4$ was added to the resulting solution, complex **3** precipitated as a white solid. It was washed with cold MeOH, dried under vacuum, and crystallized from CH_2Cl_2/*n*-hexane at −18 °C. Yield: 25%. Anal. Found: C, 54.83; H, 5.68; N, 6.22. Calcd for $C_{40}H_{49}N_4O_2OsBP_2$: C, 54.55; H, 5.61; N, 6.36. IR (CH_2Cl_2): ν_{max} (cm^{-1}) 1937 (CO), 1606 (COMe). ^1H NMR (CD_2Cl_2, 298 K): δ_H (ppm) 8.50 (1H, d, $^3J_{HH}$ = 1.6, 3), 7.78 (1H, d, $^3J_{HH}$ = 2.0, 3′), 7.50 (8H, m, *o*), 7.08 (1H, s, 5′), 7.05 (8H, t, $^3J_{HH}$ = 7.3, *m*), 7.00 (1H, d, $^3J_{HH}$ = 2.7, 5), 6.90 (4H, t, $^3J_{HH}$ = 8.7, *p*), 6.38 (1H, d, $^3J_{HH}$ = 2.6, 4′), 6.37 (1H, d, $^3J_{HH}$ = 2.5, 4), 4.71 (2H, s, CH_2), 2.48 (3H, s, COMe), 1.11 (18H, Harris t,[12] $|^2J_{PH} + {^4J_{PH}}| = 7.2$, PMe_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_C (ppm) 240.7 (t, $^2J_{CP}$ = 7.2, COMe), 184.8 (t, $^2J_{CP}$ = 9.4, CO), 164.2 (q, $^1J_{CB}$ = 48.4, *ipso*), 149.1 (s, 3), 146.8 (s, 3′), 141 (s, 5′), 136.4 (s, *o*), 135.1 (s, 5), 126.5 (s, *m*), 122.7 (s, *p*), 109.1 (s, 4′), 108 (s, 4), 65.6 (s, CH_2), 61.9 (s, COMe), 15.0 (Harris t, $|^1J_{CP} + {^3J_{CP}}| = 34.3$, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_P (ppm) − 26.8 (s, PMe_3).

***trans*-[Os(COMe)((pz)$_3$CH-κ^2)(CO)(PMe$_3$)$_2$]$^+$[BPh$_4$]$^-$ (4).** Complex **1** (50 mg, 0.093 mmol) and $Ag(CF_3SO_3)$ (21 mg, 0.08 mmol) were dissolved in 2 mL of MeOH. After 20 min the precipitated AgI was filtered off. The $(pz)_3CH$ (20 mg, 0.140 mmol) dissolved in 2 mL of MeOH was added to the remaining solution. A large excess of $NaBPh_4$ was added after 60 min and compound **4** precipitated. It was washed with cold MeOH and crystallized from CH_2Cl_2/*n*-hexane at −18 °C. Yield: 18%. Anal. Found: C, 54.69; H, 5.26; N, 8.60. Calcd for $C_{43}H_{51}N_6O_2OsBP_2$: C, 54.55; H, 5.43; N, 8.88. IR (*n*-hexane): ν_{max} (cm^{-1}) 1934 (CO), 1579 (COMe). ^1H NMR (CD_2Cl_2, 298 K): δ_H (ppm) 9.56 (1H, d, $^3J_{HH}$ = 2.5, 3), 8.05 (1H, d, $^3J_{HH}$ = 2.1, 3′), 7.56 (1H, d, $^3J_{HH}$ = 1.6, 3″), 7.30 (8H, m, *o*), 7.11 (1H, d, $^3J_{HH}$ = 3, 5′), 7.09 (1H, d, $^3J_{HH}$ = 2.9, 5), 7.0 (8H, t, $^3J_{HH}$ = 7.35, *m*), 6.99 (1H, s, CH), 6.89 (4H, t, $^3J_{HH}$ = 7.2, *p*), 6.58 (1H, dd, $^3J_{HH}$ = 2.2, $^3J_{HH}$ = 2.8, 4), 6.56 (1H, dd, $^3J_{HH}$ = 3.0, $^3J_{HH}$ = 2.6, 4′), 6.38 (1H, dd, $^3J_{HH}$ = 1.8, $^3J_{HH}$ = 2.6, 4"), 6.20 (1H, d, $^3J_{HH}$ = 2.6, 5″), 2.44 (3H, s, COMe), 0.99 (9H, Harris t, $|^2J_{PH+} {^4J_{PH}}| = 7.74$, PMe_3^B), 0.97 (9H, Harris t, $|^2J_{PH} + {^4J_{PH}}| = 7.16$, PMe_3^A). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_C (ppm) 239 (t, $^2J_{CP}$ = 7.5, COMe), 184.3 (t, $^2J_{CP}$ = 9.7, CO), 164.0 (q, $^1J_{CB}$ = 49.3, *ipso*), 153.2 (s, 3), 150 (s, 3′), 142.9 (s, 3″), 142.0 (s, 5), 139.7 (s, 5′), 136.4 (s, *o*), 129.3 (s, 5″), 126.3 (s, *m*), 122.6 (s, *p*), 110.3 (s, 4′), 110.0 (s, 4″), 109.3 (s, 4), 81.0 (s, CH), 54.2 (s, COMe), 14.9 (dd, $^1J_{CP}$ = 20.2, $^3J_{CP}$ =12.9, PMe_3^B), 14.5 (dd, $^1J_{CP}$ = 22.5, $^3J_{CP}$ = 13.4, PMe_3^A). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_P (ppm) −25.2 and −26.8 (AB system, $^2J_{PP}$ = 251.6, PMe_3^A and PMe_3^B).

[(Me)(CO)$_2$(PMe$_3$)$_2$Os(μ-I)Ag((pz)$_3$CH)]$^+$[X]$^-$ (X$^-$ = CF$_3$SO$_3^-$ (5), BF$_4^-$ (6)). Complex **1** (250 mg, 0.45 mmol) and $(pz)_3CH$ (150 mg, 0.70 mmol) were dissolved in 8 mL of MeOH. AgX (0.42 mmol) was added to the solution. Immediately, complexes **5** ($X^- = CF_3SO_3^-$) or **6** ($X^- = BF_4^-$) precipitated. They were washed with cold methanol, dried under vacuum and crystallized from CH_2Cl_2/MeOH.

Complex **5**: yield 81%. Anal. Found: C, 23.64; H, 3.0; N, 8.2. Calcd for $C_{20}H_{31}N_6O_5OsAgF_3IP_2S$: C, 23.75; H, 3.09; N, 8.31. IR (CH_2Cl_2): ν_{max} (cm^{-1}) 2018, 1949 (CO). ^1H NMR (CD_2Cl_2, 233 K): δ_H (ppm) 9.49 (1H, s, CH), 8.33 (3H, d, $^3J_{HH}$ = 2.2, 5), 7.64 (3H, d, $^3J_{HH}$ = 1.9, 3), 6.38 (3H, dd, $^3J_{HH}$ = 2.5, $^3J_{HH}$ = 2.0, 4), 1.81 (18H, Harris t, $|^2J_{PH} + {^4J_{PH}}| = 8.0$, PMe_3), 0.36 (3H, t, $^3J_{PH}$ = 8.6, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ_P (ppm) −49.3 (s, PMe_3). ^{19}F NMR (CD_2Cl_2, 298 K): δ_F (ppm) − 79.3 (s, $SO_3CF_3^-$).

Complex **6**: yield 78%. Anal. Found: C, 27.63; H, 3.5; N, 9.0. Calcd for $C_{19}H_{31}N_6O_2OsAgBF_4IP_2$: C, 27.04; H, 3.29; N, 8.85. IR (CH_2Cl_2): ν_{max} (cm^{-1}) 2018, 1949 (CO). ^1H NMR (CD_2Cl_2, 298 K): δ_H (ppm) 9.00 (1H, s, CH), 8.16 (3H, d, $^3J_{HH}$ = 2.6, 5), 7.64 (3H, d, $^3J_{HH}$ = 1.9, 3), 6.4 (3H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 1.9, 4), 1.86 (18H, Harris t, $|^2J_{PH} + {^4J_{PH}}| = 8.5$, PMe_3), 0.42 (3H, t, $^3J_{PH}$ = 8.5, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_C (ppm) 178.3 (t, $^2J_{CP}$ = 6.2, CO^A), 177.0 (t, $^2J_{CP}$ = 8.5, CO^B), 142.8 (s, 3), 132.5 (s, 5), 107.1 (s, 4), 79.1 (s, CH); 16.8 (Harris t, $|^1J_{CP} + {^3J_{CP}}| = 37.4$, PMe_3), −18 (t, $^2J_{CP}$ = 7.9, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ_P (ppm) − 51.6 (s, PMe_3). ^{19}F NMR (CD_2Cl_2, 298 K): δ_F (ppm) − 150.2 (s, BF_4^-).

***cis,trans*-[Os(Me)(MeOH)(CO)$_2$(PMe$_3$)$_2$]$^+$[BPh$_4$]$^-$ (7).** Complex **1** (300 mg, 0.54 mmol) and $AgCF_3SO_3$ (127 mg, 0.48 mmol) were dissolved in 6 mL of MeOH. The solution was stirred at room temperature for 48 h until the precipitation of AgI was completed. AgI was filtered off, and a large excess of $NaBPh_4$ was added. Complex **7** that precipitated as a white solid (yield 45%) was washed with cold methanol. Anal. Found: C, 53.9; H, 6.1. Calcd for $C_{34}H_{45}O_3OsBP_2$: C, 53.4; H, 5.93. IR (acetone): ν_{max} (cm^{-1}) 2024, 1956 (CO). ^1H NMR (acetone-d_6, 298 K): δ_H (ppm) 7.36 (8H, m, *o*), 6.95 (8H, t, $^3J_{HH}$ = 7.3, *m*), 6.80 (4H, t, $^3J_{HH}$ = 7.1, *p*), 3.84 (3H, s, *Me*OH), 1.80 (18H, Harris t, $|^2J_{PH} + {^4J_{PH}}| = 8.2$, PMe_3), 0.12 (3H, t, $^3J_{PH}$ = 8.6, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6, 298 K): δ_C (ppm) 179.5 (t, $^2J_{CP}$ = 8.4, CO^A), 178.7 (t, $^2J_{CP}$ = 8.6, CO^B), 164.5 (m, $^1J_{C^{11}B}$ = 49.1, $^1J_{C^{10}B}$ = 16.4, *ipso*), 136.5 (q, $^2J_{C^{11}B}$ = 1.3, *o*), 125.4 (q, $^3J_{C^{11}B}$ = 2.8, *m*), 121.8 (s, *p*), 13.9 (Harris t, $|^1J_{CP} + {^3J_{CP}}| = 36.4$, PMe_3), −12.1 (t, $^2J_{CP}$ = 7.7, Me). $^{31}P\{^1H\}$ NMR (acetone-d_6, 298 K): δ_P (ppm) − 30.0 (s, PMe_3).

When complex **7** is left in the NMR tube, it partially transforms into the complexes *cis,trans*-[Os(Me)(H$_2$O)(CO)$_2$(PMe$_3$)$_2$]$^+$[BPh$_4$]$^-$ (**8**) and *cis,trans*-[Os(Me)(Me$_2$CO)(CO)$_2$(PMe$_3$)$_2$]$^+$[BPh$_4$]$^-$ (**9**). Data for complex **8** are as follows. ^1H NMR (acetone-d_6, 298 K): δ_H (ppm) 1.73 (18H, Harris t, $|^2J_{PH} + {^4J_{PH}}| = 8.3$, PMe_3), 0.30 (3H, t, $^3J_{PH}$ = 8.6, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6, 298 K): δ_C (ppm) 181.2 (t, $^2J_{CP}$ = 5.7, CO^A), 179.3 (t, $^2J_{CP}$ = 8.4, CO^B), 14.0 (Harris t, $|^1J_{CP} + {^3J_{CP}}| = 37.0$, PMe_3),

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−7.9 (t, $^2J_{\mathrm{CP}} = 7.7$, Me). ^{31}P{^{1}H} NMR (acetone-d_6, 298 K): δ_{P} (ppm) −30.5 (s, $\mathrm{PMe_3}$). Data for complex **9** are as follows. ^{1}H NMR (acetone-d_6, 298 K): δ_{H} (ppm) 1.76 (18H, Harris t, $|^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}| = 8.2$, $\mathrm{PMe_3}$), 0.17 (t, $^3J_{\mathrm{PH}} = 8.6$, Me).^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ_{C} (ppm) 181.5 (t, $^2J_{\mathrm{CP}} = 6.2$, $\mathrm{CO^A}$), 180.7 (t, $^2J_{\mathrm{CP}} = 6.3$, $\mathrm{CO^B}$), 14.2 (Harris t, $|^1J_{\mathrm{CP}} + {}^3J_{\mathrm{CP}}| = 36.5$, $\mathrm{PMe_3}$), −11.6 (t, $^2J_{\mathrm{CP}} = 7.8$, Me).^{31}P{^{1}H} NMR (acetone-d_6, 298 K): δ_{P} (ppm) − 30.9 (s, $\mathrm{PMe_3}$).

***cis*-[Os(COMe)((pz)$_2$CH$_2$)(CO)$_2$(PMe$_3$)]$^+$[BPh$_4$]$^-$ (10).** Complex **2** (50 mg, 0.101 mmol) and Ag($\mathrm{CF_3SO_3}$) (19 mg, 0.07 mmol) were dissolved in 4 mL of MeOH. AgI started to precipitate immediately, and after 15 min it was filtered off. Solid $\mathrm{(pz)_2CH_2}$ (18 mg, 0.122 mmol) was then added, and the solution was stirred for 2 days at room temperature. When $\mathrm{NaBPh_4}$ was added to the resulting solution, complex **10** precipitated as a white solid. It was washed with cold MeOH and dried under vacuum. Yield: 28%. Anal. Found: C, 54.95; H, 4.68; N, 6.53. Calcd for $\mathrm{C_{38}H_{40}N_4O_3OsBP}$: C, 54.81; H, 4.84; N, 6.72. IR ($\mathrm{CH_2Cl_2}$): ν_{max} (cm^{-1}) 2048, 1979 (CO), 1608 (COMe). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{H} (ppm) 8.73 (1H, d, $^3J_{\mathrm{HH}} = 2.3$, 3), 7.66 (1H, d, $^3J_{\mathrm{HH}} = 2.1$, 3′), 7.48 (8H, m, *o*), 7.06 (8H, t, $^3J_{\mathrm{HH}} = 7.4$, *m*), 7.03 (1H, d, $^3J_{\mathrm{HH}} = 2.7$, 5′), 7.01 (1H, d, $^3J_{\mathrm{HH}} = 2.8$, 5), 6.91 (4H, t, $^3J_{\mathrm{HH}} = 8.7$, *p*), 6.44 (1H, t, $^3J_{\mathrm{HH}} = 2.6$, 4′), 6.40 (1H, dd, $^3J_{\mathrm{HH}} = 2.7$, $^3J_{\mathrm{HH}} = 2.3$, 4), 4.85 (1H, d, $^2J_{\mathrm{HH}} = 15.0$, $\mathrm{CH_2{}^A}$), 4.54 (1H, d, $^2J_{\mathrm{HH}} = 15.0$, $\mathrm{CH_2{}^B}$), 2.66 (3H, s, COMe), 1.07 (9H, d, $^2J_{\mathrm{PH}} = 9.8$, $\mathrm{PMe_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{C} (ppm) 227.4 (d, $^2J_{\mathrm{CP}} = 8.1$, COMe), 179.5 (d, $^2J_{\mathrm{CP}} = 10.7$, $\mathrm{CO^A}$), 177.7 (d, $^2J_{\mathrm{CP}} = 91.3$, $\mathrm{CO^B}$), 164.3 (q, $^1J_{\mathrm{CB}} = 48.4$, *ipso*), 147.8 (s, 3), 147.3 (s, 3′), 137.5 (s, 5′), 136.3 (s, *o*), 136.1 (s, 5), 126.5 (s, *m*), 122.7 (s, *p*), 109.3 (s, 4′), 108.4 (s, 4), 62.6 (s, $\mathrm{CH_2}$), 55.1 (s, COMe), 13.1 (d, $^1J_{\mathrm{CP}} = 34.7$, $\mathrm{PMe_3}$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{P} (ppm) −26.4 (s, $\mathrm{PMe_3}$).

***cis*-[Os(COMe)((pz)$_3$CH-κ^2)(CO)$_2$(PMe$_3$)]$^+$[BPh$_4$]$^-$ (11).** Complex **2** (33 mg, 0.067 mmol) and Ag($\mathrm{CF_3SO_3}$) (12 mg, 0.048 mmol) were dissolved in 4 mL of MeOH. AgI started to precipitate immediately, and after 15 min it was filtered off. Solid $\mathrm{(pz)_3CH}$ (16 mg, 0.077 mmol) was then added, and the solution was stirred for 2 days. When $\mathrm{NaBPh_4}$ was added to the resulting solution, complex **11** precipitated as a white solid. It was washed with cold MeOH and dried under vacuum. Yield: 56%. Anal. Found: C, 54.96; H, 4.56; N, 9.20. Calcd for $\mathrm{C_{41}H_{42}N_6O_3OsBP}$: C, 54.79; H, 4.71; N, 9.35. IR ($\mathrm{CH_2Cl_2}$): ν_{max} (cm^{-1}) 2054, 1981 (CO), 1606 (COMe). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{H} (ppm) 9.15 (1H, dd, $^3J_{\mathrm{HH}} = 2.4$, $^4J_{\mathrm{HH}} = 0.6$, 3), 7.82 (1H, d, $^3J_{\mathrm{HH}} = 2.2$, 3′), 7.57 (1H, d, $^3J_{\mathrm{HH}} = 1.7$, 3″), 7.42 (8H, m, *o*), 7.23 (1H, d, $^3J_{\mathrm{HH}} = 2.9$, 5′), 7.18 (1H, d, $^3J_{\mathrm{HH}} = 2.9$, 5), 6.98 (8H, t, $^3J_{\mathrm{HH}} = 7.4$, *m*), 6.78 (4H, t, $^3J_{\mathrm{HH}} = 7.2$, *p*), 6.58 (1H, t, $^3J_{\mathrm{HH}} = 2.5$, 4), 6.54 (1H, dd, $^3J_{\mathrm{HH}} = 2.8$, $^3J_{\mathrm{HH}} = 2.2$, 4′), 6.43 (1H, dd, $^3J_{\mathrm{HH}} = 1.8$, $^3J_{\mathrm{HH}} = 2.6$, 4″), 6.40 (1H, s, CH), 6.05 (1H, d, $^3J_{\mathrm{HH}} = 2.6$, 5″), 2.54 (3H, s, COMe), 1.09 (9H, d, $^2J_{\mathrm{PH}} = 9.9$, $\mathrm{PMe_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{C} (ppm) 228.5 (d, $^2J_{\mathrm{CP}} = 7.7$, COMe), 179.4 (d, $^2J_{\mathrm{CP}} = 10.8$, $\mathrm{CO^A}$), 175.9 (d, $^2J_{\mathrm{CP}} = 94.3$, $\mathrm{CO^B}$), 164.2 (q, $^1J_{\mathrm{CB}} = 49.2$, *ipso*), 150.0 (s, 3), 149.7 (s, 3′), 143.2 (s, 3″), 141.8 (s, 5), 140.1 (s, 5′), 136.2 (s, *o*), 128.4 (s, 5″), 126.5 (s, *m*), 122.7 (s, *p*), 110.5 (s, 4′), 110.0 (s, 4″), 109.0 (s, 4), 80.6 (s, CH), 54.7 (s, COMe), 13.1 (d, $^1J_{\mathrm{CP}} = 34.7$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ_{P} (ppm) −25.0 (s, $\mathrm{PMe_3}$).

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Supporting Information Available: Crystal data and structure refinement for **8** (Table 1s), atomic coordinates (Table 2s), H-atom coordinates (Table 3s), anisotropic thermal parameters (Table 4s), and all bond lengths and angles (Table 5s). This material is available free of charge via the Internet at http://pubs.acs.org.

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