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Notes

Preparation of Diazoalkane Complexes of Osmium(II)

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Introduction

Diazoalkanes are interesting molecules which have been used in inorganic or organometallic chemistry as precursors of metal carbene complexes[1−3] or to coordinate the central metal to give the corresponding diazoalkane derivatives.[1,3−5] The interaction of a $RR'CN_2$ species with a transition metal complex may, in fact, proceed either with loss of N_2, to give a carbene species which may or may not be stabilized by the metal, or with coordination of the intact diazo molecule. Diazoalkane complexes may also be obtained from reactions of dinitrogen derivatives.[6]

Interest in this area has been stimulated by the various coordination modes that the diazoalkane ligand may present (η^1, η^2, μ, etc.)[1,4,5] and by the influence that coordination may have on the reactivity of $RR'CN_2$ species.[1,4,5] Also of interest is the importance of diazoalkane complexes as models in the chemistry of N_2 fixation.[1,6,7] However, a comparison of the literature data showed that diazoalkane derivatives are far less studied than the related "diazo" complexes[1,7] such as aryldiazenido and aryldiazene, and relatively few complexes have been synthesized.[4,5,8]

We recently reported[9,10] the synthesis and reactivity of aryldiazene, aryldiazenido, hydrazine and dinitrogen derivatives of the iron family of the types $[MH(ArN{=}NH)P_4]^+$, $[M(ArN{=}NH_2)P_4]^{2+}$, $[M(ArN_2)P_4]^+$, $[M(RNHNH_2)_2P_4]^{2+}$ (M = Fe, Ru, Os), $[OsH(N_2)P_4]^+$, and $[Fe(ArN_2)(CO)_2P_2]^+$ (P = phosphite). We have now extended these studies to include diazoalkane as ligand, and this paper reports the synthesis and characterization of the first mononuclear[2d] diazoalkane complexes of osmium.

Experimental Section

All synthetic work was carried out in an inert atmosphere (argon, N_2) using standard Schlenk techniques or a Vacuum Atmospheres drybox. Once isolated, the complexes turned out to be quite air-stable and were stored at −20 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Phosphites $PPh(OEt)_2$, PPh_2OEt, and PPh_2OMe were prepared by the method of Rabinowitz and Pellon.[11] $(CH_3)_3SiCHN_2$ and $C_2H_5CO_2CHN_2$ species were Aldrich products used as received. The other diazoalkanes, $4\text{-}ClC_6H_4CHN_2$, $(C_6H_5)_2CN_2$, $C_6H_5(C_6H_5CO)CN_2$, $C_6H_5(4\text{-}CH_3C_6H_4)CN_2$, $C_6H_5(C_5H_5N)CN_2$, and $C_{12}H_8CN_2$ (9-diazofluorene) were prepared according to literature procedures.[12] *p*-Tolyl isocyanide was obtained by the method of Ziehn

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et al.[13] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Digilab Bio-Rad FTS-40 or Nicolet Magna 750 FT-IR spectrophotometers. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise stated. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SwaN-MR software package was used to treat NMR data.[14] The conductivity of 10^{-3} M solutions of the complexes in $MeNO_2$ at 25 °C was measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. Hydrides OsH_2P_4 [P = PPh(OEt)$_2$, PPh$_2$OEt, PPh$_2$OMe] were prepared following the reported method.[10a,c]

[OsH(N$_2$CHR)P$_4$]CF$_3$SO$_3$ (1, 2, 3) [P = PPh(OEt)$_2$ (1), PPh$_2$OEt (2), PPh$_2$OMe (3); R = CO$_2$C$_2$H$_5$ (a), (CH$_3$)$_3$Si (b), 4-ClC$_6$H$_4$ (c)]. To a solution of the hydride OsH_2P_4 (0.10 mmol) in 10 mL of toluene cooled to −196 °C was added an equimolar amount of $CF_3SO_3CH_3$ (0.10 mmol, 11.2 μL), and the reaction mixture, brought to room temperature, was stirred for 90 min. An excess of the appropriate diazoalkane (0.30 mmol) in 5 mL of toluene or hexane (1.5 mL) was added to the solution, which was vigorously stirred until a solid separated out (10−20 min). After 1 h, the solid was filtered, washed with diethyl ether, and dried under vacuum; yield was between 40 and 50%.

[OsH(N$_2$CRR′)P$_4$]CF$_3$SO$_3$ (1, 2, 3) [P = PPh(OEt)$_2$ (1), PPh$_2$OEt (2), PPh$_2$OMe (3); R = R′ = Ph (d); R = Ph, R′ = 4-CH$_3$C$_6$H$_4$ (e); R = Ph, R′ = C$_6$H$_5$CO (f); RR′ = C$_{12}$H$_8$ (g); R = Ph, R′ = C$_5$H$_5$N (h)]. These complexes were prepared exactly like the related compounds containing the monosubstituted $RHCN_2$ diazoalkanes but using a shorter reaction time (40−50 min), which gave a higher yield (50−70%).

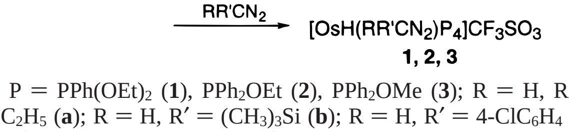
[OsH(SO$_2$)P$_4$]BPh$_4$ [P = PPh(OEt)$_2$ (4), PPh$_2$OEt (5)]. A solution of $[OsH(N_2CC_{12}H_8)P_4]CF_3SO_3$ (0.12 mmol) in 10 mL of CH_2Cl_2 was allowed to stand under SO_2 (1 atm) for 30 min. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (3 mL). The addition of an excess of $NaBPh_4$ (0.24 mmol, 82 mg) in 2 mL of ethanol to the resulting solution caused the separation of a yellow-green solid, which was filtered and crystallized from ethanol; yield ≥ 70%.

Results and Discussion

A series of diazoalkane complexes $[OsH(N_2CRR')P_4]CF_3SO_3$ (**1**−**3**) was prepared by reacting hydride species OsH_2P_4 first with methyl triflate and then with an excess of diazoalkane $RR'CN_2$, as shown in Scheme 1.

The reaction of OsH_2P_4 with methyl triflate proceeds with the evolution of CH_4 (by NMR) and probable formation[15] of $OsH(\eta^1\text{-}OSO_2CF_3)P_4$. η^1-Triflate is a labile ligand in the compound and may easily be substituted by the diazoalkane molecule, affording the final $[OsH(N_2CRR')P_4]CF_3SO_3$ (**1**−**3**) derivatives. Alternatively, diazoalkane complexes **2** and **3** may also be prepared by displacement of the N_2 ligand with $RR'CN_2$ in the $[OsH(N_2)P_4]CF_3SO_3$ derivatives.[10a] Instead, the related $[OsH(\eta^2\text{-}H_2)P_4]^+$ cations[10a,b] are unreactive toward the $RR'CN_2$ molecule and cannot be used as precursors.

Scheme 1[a]



[a] P = PPh(OEt)$_2$ (**1**), PPh$_2$OEt (**2**), PPh$_2$OMe (**3**); R = H, R′ = CO$_2$C$_2$H$_5$ (**a**); R = H, R′ = (CH$_3$)$_3$Si (**b**); R = H, R′ = 4-ClC$_6$H$_4$ (**c**); R = R′ = C$_6$H$_5$ (**d**); R = C$_6$H$_5$, R′ = 4-CH$_3$C$_6$H$_4$ (**e**); R = C$_6$H$_5$, R′ = C$_6$H$_5$CO (**f**); RR′ = C$_{12}$H$_8$ (**g**); R = C$_6$H$_5$, R′ = C$_5$H$_5$N (**h**).

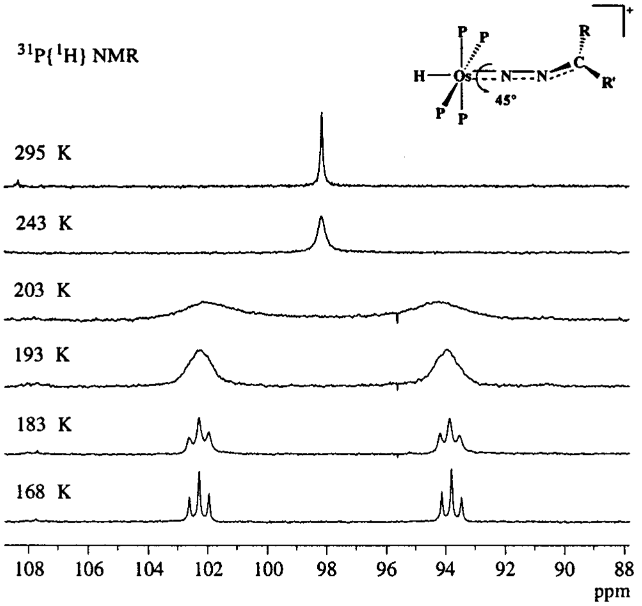


Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra in CD_2Cl_2 of $[OsH(N_2CC_{12}H_8)(PPh_2OEt)_4]CF_3SO_3$ (**2g**).

Good analytical data were obtained for all complexes **1**−**3** which are relatively air-stable, green to brown solids, and soluble in polar organic solvents, in which they behave as 1:1 electrolytes.[16] The IR and NMR spectra (Table 1) confirm the proposed formulation. The IR spectra show a medium- or strong-intensity band at 1992−2100 cm^{-1}, attributed to the νN_2 of the diazoalkane ligand. Its value also suggests[5] a singly bent geometry for the $RR'CN_2$ group. However, in some complexes, this band is of very low intensity or completely absent, although elemental analyses and NMR data indicate the presence of the $RR'CN_2$ moiety. This fact had already been observed in other diazoalkane complexes[4,5] and may be explained[5e] by the competition between the metal and the substituents at the N=N groups for π donation into nitrogen antibonding orbitals. This competition probably has the net effect of making the electron density of these two nitrogen atoms nearly equivalent, with a resulting small dipole, which presumably also makes the change in dipole moment during the vibration small.

The IR spectra also show the bands characteristic of the substituents of the diazoalkane and, for some complexes, weak absorption at 2125−2100 cm^{-1}, due to stretching of the Os−H bond.

In the low-frequency region, the ^{1}H NMR spectra show a well-resolved quintet between −8.21 and −13.6 ppm, attributed to the hydride ligand coupled with four equivalent phosphorus nuclei. The spectra also reveal the signals of the phosphite ligand and the substituents at the N=N group of the diazoalkane ligand, in agreement with the proposed formulation.

At room temperature, the ^{31}P{^{1}H} NMR spectra of all complexes **1**−**3** appear as sharp singlets, suggesting the mutually trans position of the hydride and the $RR'CN_2$ ligand. However, lowering of sample temperature causes a change in the spectra of all the diazoalkane complexes and, in some cases, the spectra resolve at −80 °C in A_2B_2-type multiplets. Figure 1 shows an

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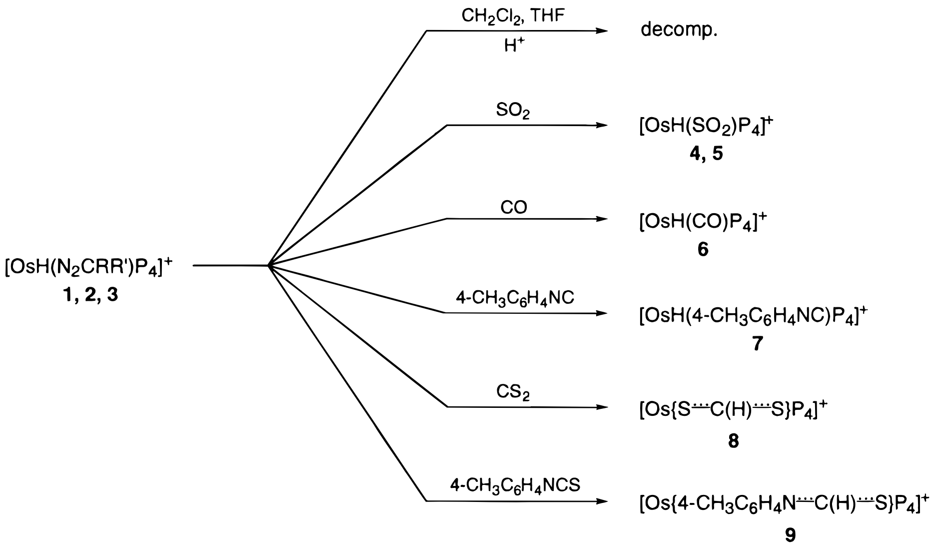
Table 1. IR and NMR Spectroscopic Data for the Diazoalkane Complexes

no.	compound	IR^a (cm^{-1})	assgnt	^{1}H NMR^{b,c} (ppm; J, Hz)	assgnt	spin syst	^{31}P{^{1}H} NMR^{b,d} (ppm; J, Hz)
1a	$[\mathrm{OsH\{N_2C(H)COOEt\}\{PPh(OEt)_2\}_4]CF_3SO_3}$	2100 w	ν(OsH)	4.25 q	CH_2 diaz	A_4	116.9 s
		2050 m	$\nu(N_2)$	3.91 s	CH		116.0 m^e
		1674 s	ν(CO)	3.66, 3.48 m	CH_2 phos		
				1.31 t	CH_3 diaz		
				1.15 t	CH_3 phos		
				−11.38 qi	H hydride		
				$J_{PH} = 20$			
1f	$[\mathrm{OsH\{N_2C(C_6H_5)COC_6H_5\}\{PPh(OEt)_2\}_4]CF_3SO_3}$	2100 m	$\nu(N_2)$	3.55, 3.41 m	CH_2	A_4	115.3 s
				1.04 t	CH_3		
				−11.02 qi	H hydride		
				$J_{PH} = 20$			
1g	$[\mathrm{OsH\{N_2CC_{12}H_8\}\{PPh(OEt)_2\}_4]CF_3SO_3}^f$	2110 w	ν(OsH)	3.80−3.50 m	CH_2	A_4	115.6 s
		2009 m	$\nu(N_2)$	1.20 t	CH_3		
				−10.84 qi	H hydride		
				$J_{PH} = 20$			
2a	$[\mathrm{OsH\{N_2C(H)COOEt\}\{PPh_2OEt\}_4]CF_3SO_3}$	2110 w	ν(OsH)	4.37 br	CH_2 diaz	A_4	101.5 s
		1675 s	ν(CO)	4.00 s	CH		100.7 m^e
				3.04 m	CH_2 phos		
				1.42 t	CH_3 diaz		
				0.29 t	CH_3 phos		
				−9.87 qi	H hydride		
				$J_{PH} = 20$			
2b	$[\mathrm{OsH\{N_2C(H)Si(CH_3)_3\}\{PPh_2OEt\}_4]CF_3SO_3}$	2055 m	$\nu(N_2)$	3.02 br	CH_2	A_4	101.6 s
				0.38 s	CH_3 diaz		100.4 m, br^e
				0.32 t	CH_3 phos		
				−13.6 qi	H hydride		
				$J_{PH} = 20$			
2c	$[\mathrm{OsH\{N_2C(H)\text{-}4\text{-}ClC_6H_4\}\{PPh_2OEt\}_4]CF_3SO_3}$			3.76 s	CH	A_4	101.8 s
				3.02 m	CH_2		101.0 m^e
				0.30 t, br	CH_3		
				−10.80 qi	H hydride		
				$J_{PH} = 20$			
2d	$[\mathrm{OsH\{N_2C(C_6H_5)_2\}\{PPh_2OEt\}_4]CF_3SO_3}$	1992 m	$\nu(N_2)$	2.98 br	CH_2	A_4	99.7 s
				0.40 t	CH_3	$A_2B_2{}^e$	$\delta_A = 103.7$
				−11.07 qi	H hydride		$\delta_B = 94.4$
				$J_{PH} = 20$			$J_{AB} = 27$
2e	$[\mathrm{OsH\{N_2C(C_6H_5)\text{-}4\text{-}CH_3C_6H_4\}\{PPh_2OEt\}_4]CF_3SO_3}$	2125 w	ν(OsH)	2.98 br	CH_2	A_4	99.8 s
		1995 m	$\nu(N_2)$	2.47 s	CH_3 diaz	$A_2B_2{}^e$	$\delta_A = 104.2$
				0.41 t	CH_3 phos		$\delta_B = 95.3$
				−11.17 qi	H hydride		$J_{AB} = 27$
2f	$[\mathrm{OsH\{N_2C(C_6H_5)COC_6H_5\}\{PPh_2OEt\}_4]CF_3SO_3}$	2115 w	ν(OsH)	3.06 m	CH_2	A_4	98.4 s
		1595 m	ν(CO)	0.42 t	CH_3		
				−9.49 qi	H hydride		
				$J_{PH} = 20$			
2g	$[\mathrm{OsH\{N_2CC_{12}H_8\}\{PPh_2OEt\}_4]CF_3SO_3}^f$	2013 m	$\nu(N_2)$	3.04 m, br	CH_2	A_4	98.2 s
				0.42 t	CH_3	$A_2B_2{}^g$	$\delta_A = 102.3$
				−9.15 qi	H hydride		$\delta_B = 93.8$
				$J_{PH} = 20$			$J_{AB} = 27$
2h	$[\mathrm{OsH\{N_2C(C_6H_5)C_5H_5N\}\{PPh_2OEt\}_4]CF_3SO_3}$	2105 w	ν(OsH)	2.99 br	CH_2	A_4	96.4 s
				0.36 t	CH_3		100.6, 92.2 br^e
				−8.21 qi	H hydride		
				$J_{PH} = 20$			
3a	$[\mathrm{OsH\{N_2C(H)COOEt\}\{PPh_2OMe\}_4]CF_3SO_3}$	1669 s	ν(CO)	4.23 q	CH_2	A_4	104.4 s
				3.75 s	CH		104.9 m, br^e
				1.31 t	CH_3 diaz		
				2.58 d	CH_3 phos		
				−9.98 qi	H hydride		
				$J_{PH} = 20$			
3g	$[\mathrm{OsH\{N_2CC_{12}H_8\}\{PPh_2OMe\}_4]CF_3SO_3}^f$	2013 s	$\nu(N_2)$	2.68 d	CH_3	A_4	101.0 s
				−9.22 qi	H hydride		
				$J_{PH} = 20$			
4	$[\mathrm{OsH(SO_2)\{PPh(OEt)_2\}_4]BPh_4}$	2052 w	ν(OsH)	3.64 m	CH_2	A_4	113.1 s
		1268 m	$\nu(SO_2)$	1.18 t	CH_3		
		1121 m		−9.06 qi	H hydride		
				$J_{PH} = 20$			
5	$[\mathrm{OsH(SO_2)\{PPh_2OEt\}_4]BPh_4}$	2062 w	ν(OsH)	3.22 m	CH_2	A_4	93.7 s
		1267 m	$\nu(SO_2)$	0.79 t	CH_3		93.0 s^h
		1114 m		−7.42 qi	H hydride		
				$J_{PH} = 20$			

[a] In KBr. [b] In CD_2Cl_2 at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] At −90 °C. [f] $N_2CC_{12}H_8$ = 9-diazofluorene. [g] At −105 °C. [h] At −70 °C.

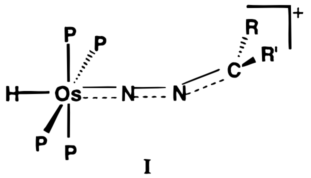
Scheme 2[a]



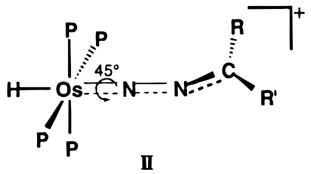
[a] P = $PPh(OEt)_2$ (**4**), PPh_2OEt (**5**).

example of variable-temperature ^{31}P spectra. The proton spectra also change with temperature, and at −80 °C the hydride signal appears as a multiplet (A_2B_2X-type spectra). However, some complexes, such as those containing a monosubstituted diazoalkane ligand, i.e., $[OsH\{N_2C(H)R\}P_4]^+$ (**1a**, **2a**−**c**, **3a**) and $[OsH\{N_2C(C_6H_5)C_5H_5N\}P_4]CF_3SO_3$ (**2h**), do show a complicated multiplet which does not resolve even at −90 °C. The spectra are not symmetric, but in the absence of low-exchange conditions no conclusion regarding the type of spectra (A_2B_2, AB_2C, ABC_2, etc.) can be made.

These results may be interpreted on the basis of the existence of a singly bent diazoalkane ligand whose restricted rotation around the OsNN axis makes the phosphorus atoms magnetically inequivalent. In fact, the diazoalkane ligand can be oriented with the N−N−C plane eclipsing an equatorial bond of the octahedral geometry (see structure **I**) or over a P−Os−P bisector, as in structure **II**.



I



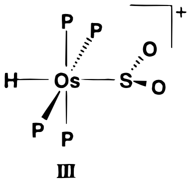
II

The ^{31}P spectrum of limit geometry **I** is expected as an ABC_2 or AB_2C multiplet, whereas that of the structure in which the plane of the diazoalkane bisects the P−Os−P angle (**II**) should be a symmetric A_2B_2-type multiplet. Our low-exchange spectra appear as A_2B_2 multiplets and suggest a type-**II** geometry. Even rotation around the NC axis still present at −80 °C should not change the profiles of the spectra, and therefore, although the absence of a crystal structure does not allow conclusive assignment, the ^{31}P data suggest the presence in solution of a bent diazoalkane ligand oriented over a P−Os−P bisector, as in geometry **II**.

Some studies on the reactivity of diazoalkane complexes **1**−**3** were undertaken, and the results are summarized in Scheme 2.

In CH_2Cl_2 or other solvents, the complexes are unstable even at 0 °C and slowly decompose, affording a brown solution from which no solid compounds could be isolated. However, the NMR spectra (^1H, ^{13}C) of the resulting oil do not show the presence of a carbene complex forming from the N_2CRR' ligand by loss of N_2. The addition of HBF_4 or CF_3SO_3H to the solution increases the decomposition rate of **1**−**3**, but also in this case no carbene complexes could be detected. Treatment with CO or isocyanide proceeds with substitution of the N_2CRR' ligand, affording the known[10a,b] $[OsH(CO)P_4]^+$ (**6**) and $[OsH(4\text{-}CH_3C_6H_4NC)P_4]^+$ (**7**) cations. Also SO_2 (1 atm) gives rise to the substitution reaction, affording new sulfur dioxide $[OsH(SO_2)P_4]^+$ (**4**, **5**) derivatives, which were isolated as BPh_4^- salts and characterized. Instead, the reaction of **1**−**3** with carbon disulfide or *p*-tolyl isothiocyanate proceeds to give dithioformato **8** or *p*-tolylthioformamido **9** complexes,[17] probably the result of substitution of N_2CRR' and further insertion of the CS_2 or $4\text{-}CH_3C_6H_4NCS$ molecule into the Os−H bond.

The sulfur dioxide complexes $[OsH(SO_2)P_4]BPh_4$ (**4**, **5**) are yellow solids, stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes.[16] Spectroscopic (Table 1) and analytical data support their formulation. In particular, the IR spectra show weak bands at 2052 (**4**) or 2062 (**5**) cm^{-1}, attributed to νOsH. In the 1300−1100 cm^{-1} region, two bands of medium intensity are present at 1268 and 1121 cm^{-1} for **4** and at 1267 and 1114 cm^{-1} for **5**, attributed to the νSO of the SO_2 ligand. A comparison of these νSO values with those of structurally characterized sulfur dioxide complexes indicated coplanar MSO_2 geometry[18] for our **4**, **5** derivatives.



III

In the temperature range between +20 and −80 °C, the ^{31}P-

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(17) Albertin, G.; Antoniutti, S.; Bordignon, E. *Gazz. Chim. Ital.* **1994**, *124*, 355.

{^{1}H} NMR spectra of compounds **4** and **5** appear as sharp singlets. The proton spectra show well-resolved quintets at −9.06 (**4**) and −7.43 ppm (**5**) due to hydride ligand coupling with four equivalent phosphorus nuclei. A trans geometry **III** was therefore proposed for the unprecedented SO_2 osmium derivatives **4** and **5**.

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Supporting Information Available: The complete list of analytical data for all complexes (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182. (b) Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98.