Table II. First-Order Rate Constants for the Thermal Cis → Trans Isomerization of Azobenzene at Various Pressures

benzene[a]		n-hexane[a]	
pressure, bar	10^4k, s^{-1}	pressure, bar	10^4k, s^{-1}
1	1.00	1	1.23
600	0.99	300	1.28
1200	1.06	600	1.33
1800	1.07	900	1.33
2100	1.10	1200	1.40
		1500	1.43
		1800	1.46
		2100	1.48

[a] Solvent (60 °C).

by a conventional sampling technique. The small pressure effects observed also support the above suggestion since no major polarity change is expected during activation for this compound.

Further experiments with other solvents and with other azobenzenes are in progress.

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Carbonyl, Thiocarbonyl, Selenocarbonyl, and Tellurocarbonyl Complexes Derived from a Dichlorocarbene Complex of Osmium

Sir:

The successful coordination of the very reactive molecules carbon monosulfide[1] and carbon monoselenide[2] in transition-metal complexes suggests that it may also be possible to stabilize, through coordination, the unknown molecule carbon monotelluride. Most synthetic routes to carbon monosulfide (or thiocarbonyl) complexes and carbon monoselenide (or selenocarbonyl) complexes involve the use of carbon disulfide (or thiophosgene) and carbon diselenide, respectively. Since the tellurium analogues of these starting materials, i.e., carbon ditelluride and tellurophosgene are also unknown molecules, a new approach was clearly necessary for tellurocarbonyl complexes and this paper describes such an approach which depends upon an unusual dichlorocarbene complex of osmium, $OsCl_2(CCl_2)(CO)(PPh_3)_2$.

It is surprising that, although dichlorocarbene was one of the first carbenes to be recognized, no transition-metal complex of this species was reported until 1977.[3] $Fe(TPP)(CCl_2)(H_2O)$ results from the reaction of *meso*-tetraphenylporphyrinatoiron(II) [Fe(TPP)] with carbon tetrachloride in the presence of an excess of reducing agent and the thorough characterization of this molecule includes an X-ray crystal structure determination.[4] This is apparently the only dichlorocarbene complex to have been described, although various monochlorocarbene complexes are known.[5] Our synthesis of an osmium dichlorocarbene complex was a development of earlier work in which we had shown that reaction between $OsHCl(CO)(PPh_3)_3$ and a diorganomercury compound led to a coordinatively unsaturated organo derivative of osmium(II),[6] vis.,

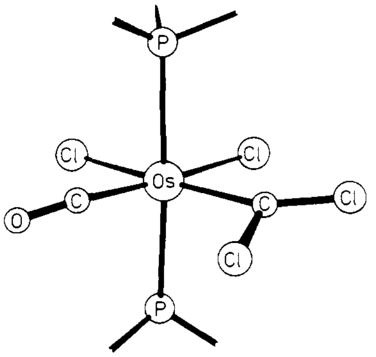
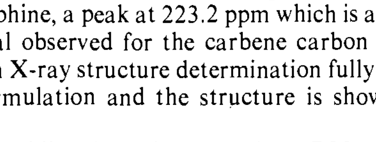


Figure 1. The inner coordination sphere of $OsCl_2(CCl_2)(CO)(PPh_3)_2$.

$$OsHCl(CO)(PPh_3)_3 + HgR_2 \rightarrow OsRCl(CO)(PPh_3)_2 + RH + Hg\downarrow + PPh_3$$

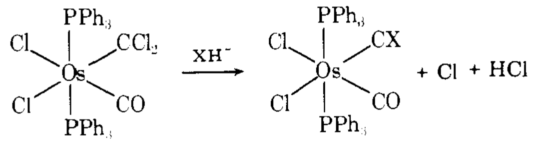
By using this reaction to transfer a trichloromethyl group to osmium, we anticipated that rearrangement of the expected coordinatively unsaturated trichloromethyl intermediate could lead to a dichlorocarbene complex.

In fact, reaction between $OsHCl(CO)(PPh_3)_3$ and $Hg(CCl_3)_2$[7] proceeded to give orange crystals of $OsCl_2(CCl_2)(CO)(PPh_3)_2$ (I) in >80% yield.[8] The dichlorocarbene ligand gives rise to IR bands at 880 (s) and 780 and 770 (m) cm^{-1} which we assign to ν(C–Cl). $Fe(TPP)(CCl_2)$ exhibits $\nu_{C\text{-}Cl}$ at 872 cm^{-1}.[4] The ^{13}C NMR spectrum ($CDCl_3$, $SiMe_4$) shows, in addition to the signals arising from triphenylphosphine, a peak at 223.2 ppm which is also very close to the signal observed for the carbene carbon in $Fe(TPP)(CCl_2)$.[3] An X-ray structure determination fully confirms the carbene formulation and the structure is shown in Figure 1.[9]



I

I reacts rapidly with primary amines, RNH_2 (R = CH_3, n-C_4H_9, p-tolyl), to form the isocyanide complexes $OsCl_2(CNR)(CO)(PPh_3)_2$ and slowly with water to form $OsCl_2(CO)_2(PPh_3)_2$.[10] I appears, therefore, to be a perfect precursor of thiocarbonyl, selenocarbonyl, and tellurocarbonyl complexes through reaction with SH^-, SeH^-,[11] and TeH^-,[12] respectively.



X = S, Se, Te

From this reaction thiocarbonyl and selenocarbonyl derivatives resulted in high yield, but the tellurocarbonyl was isolated in only 30% yield after chromatography.[13] This reduced yield is probably associated with the difficulty of preparing

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Table I. IR Data[a] for Osmium Complexes[b]

compound	ν(CO)	ν(CX)
$\mathrm{OsCl_2(CCl_2)(CO)(PPh_3)_2}$	2012, 1990	880, 780, 770
$\mathrm{OsCl_2(CNCH_3)(CO)(PPh_3)_2}$	1956	2200
$\mathrm{OsCl_2(CO)_2(PPh_3)_2}$	2040, 1975	
$\mathrm{OsCl_2(CS)(CO)(PPh_3)_2}$	2040, 2030, 2020	1315
$\mathrm{OsCl_2(CSe)(CO)(PPh_3)_2}$	2036, 2018	1156
$\mathrm{OsCl_2(CTe)(CO)(PPh_3)_2}$	2040	1046

[a] In reciprocal centimeters. Measured as Nujol mulls. [b] All compounds have satisfactory C and H analyses.

pure $\mathrm{TeH^-}$. The tellurocarbonyl complex forms orange crystals mp 221–223 °C, which are air stable. The corresponding carbonyl, thiocarbonyl, and selenocarbonyl are almost colorless. All the compounds show an exceptionally intense infrared absorption associated with $\nu_{(\mathrm{CX})}$ (see Table I) dropping from 1315 cm^{-1} for $\nu_{(\mathrm{CS})}$ to 1046 cm^{-1} for $\nu_{(\mathrm{CTe})}$. $\nu_{(\mathrm{CO})}$ remains almost constant throughout the series of compounds.

The stereochemistry of all derivatives is probably as depicted above and this has been confirmed for $\mathrm{OsCl_2(CS)(CO)(PPh_3)_2}$ by X-ray crystal structure analysis.[14] Since this is the first complete series of chalcocarbonyl compounds to be described, crystal structure determinations of all members of the series are planned to help evaluate the bonding characteristics of each ligand.

The dichlorocarbene complex promises to have diverse synthetic applications, and the further reactions of I are being studied.

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(8) $\mathrm{OsHCl(CO)(PPh_3)_3}$ (8.0 g) and $\mathrm{Hg(CCl_3)_2}$ (8.0 g) were added to rapidly stirred, boiling toluene (1.2 L) and the resulting solution heated under reflux for 25 min. The solution was then cooled in ice and filtered through a Celite pad. The toluene was removed under reduced pressure and the resulting orange oil crystallized from dichloromethane–ethanol. Recrystallization from benzene–ethanol yielded pure $\mathrm{OsCl_2(CCl_2)(CO)(PPh_3)_2}$ (5.5 g, 80%). Anal. Calcd for $\mathrm{C_{38}H_{30}Cl_4OOsP_2}$: C, 50.45; H, 3.34. Found: C, 50.90; H, 3.37.

(9) Crystal data and refinement results for $\mathrm{OsCl_2(CCl_2)(CO)(PPh_3)_2}$: orthorhombic; a = 19.225 (2), b = 16.675 (2), c = 22.078 (3) Å; space group *Pbca*; Z = 8. Intensity data were collected on a four-circle diffractometer and the structure was solved by conventional methods. Least-squares refinement, with anisotropic thermal parameters assigned to the osmium and coordinated phosphorus and chlorine atoms, has given R = 0.061 for 1476 observed reflections. The CO and $\mathrm{CCl_2}$ groups interchange between two sites, and it was necessary to refine them on the basis of a disordered model. Accordingly, their individual positions are not reliably determined. Details of the structure determination will be published elsewhere.

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(13) $\mathrm{OsCl_2(CCl_2)(CO)(PPh_3)_2}$ (1.5 g) was placed in degassed benzene (55 mL) and NaTeH solution[12] (4.8 mL) added. After the mixture was stirred 1 min, most of the benzene was removed under reduced pressure and a black solid obtained by the addition of *n*-hexane. This was chromatographed on silica gel (3 × 42 cm column) using dichloromethane as eluant; the orange band was collected and crystallized using ethanol. To remove the small amount of $\mathrm{OsCl_2(CO)_2(PPh_3)_2}$ sometimes present in the sample, the material was then dissolved in an acetonitrile–dichloromethane mixture (30:30 mL), $\mathrm{AgClO_4}$ (0.15 g) added, and the solution heated under reflux for 15 min (this converts the $\mathrm{OsCl_2(CTe)(CO)(PPh_3)_2}$ into $\mathrm{[OsCl(NCCH_3)(CTe)(CO)(PPh_3)_2]ClO_4}$, the $\mathrm{OsCl_2(CO)_2(PPh_3)_2}$ remaining unchanged). The precipitated AgCl was removed by filtration and ethanol added to the filtrate. The solvent volume was then carefully lowered under reduced pressure to effect the selective crystallization of the $\mathrm{OsCl_2(CO)_2(PPh_3)_2}$ which was removed by filtration. To the $\mathrm{[OsCl(NCCH_3)(CTe)(CO)(PPh_3)_2]ClO_4}$ in the filtrate, LiCl (0.50 g) in ethanol–water was added and the resulting orange crystals of the regenerated $\mathrm{OsCl_2(CTe)(CO)(PPh_3)_2}$ were collected and purified by chromatography on silica gel (3 × 18 cm column) using dichloromethane as eluant. The orange band was collected and crystallized using ethanol to yield pure $\mathrm{OsCl_2(CTe)(CO)(PPh_3)_2}$ (0.45 g, 28%). Anal. Calcd for $\mathrm{C_{38}H_{30}Cl_2OOsP_2Te}$: C, 47.88; H, 3.17. Found: C, 47.61; H, 3.39.

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Correlation of Circularly Polarized Luminescence Induced in Tb(dpm)$_3$ by Chiral Solvents with the Absolute Configuration of Those Solvents

Sir:

The determination of the absolute configuration of a chiral substance is a very important part of the characterization of that molecule. Considerable success has been attained by Nakanishi and Dillon[1] in absolute configurational studies of vicinal glycols with metal derivatives of β-diketones. These workers were able to correlate the sign of circular dichroism peaks appearing ~300 nm with the absolute configurations of numerous glycols and amino alcohols. Other workers have examined the circular dichroism induced in the $^7\mathrm{F}_0 \rightarrow {}^5\mathrm{D}_1$ absorption of Eu(III) when Eu(fod)$_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) adducts with chiral alcohols were prepared.[2] These methods are attractive in that the experiments are easy to carry out and the results usually adhere to the rules stated by the authors.

When a chiral molecule is also capable of luminescence after being excited by UV light, it is often possible to observe the excited-state analogue of circular dichroism, circularly polarized luminescence (CPL).[3] We have observed earlier that CPL could be induced in achiral Eu(III) β-diketonate chelates upon complexation with optically active solvents,[4] although we did not attempt to draw correlations between the configuration of the chiral solvent and the signs of the CPL. In the present work, the sign of the CPL induced in Tb(dpm)$_3$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dione) is correlated with the absolute configuration of several chiral solvents.[5]

When Tb(dpm)$_3$ is dissolved in (R)-α-phenethylamine, strong Tb(III) luminescence is observed at 545 nm, corresponding to the $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_5$ transition. This transition is partially circularly polarized, and the particular CPL line shape associated with the CPL induced by the R enantiomer is shown in Figure 1.[6] Similar line shapes (although not magnitudes) were obtained when the R isomers of 2-aminobutane, 2-aminoheptane, α-phenethyl alcohol, and propylene glycol were used as solvents for the Tb(dpm)$_3$. Two CPL extrema were observed, and in general, when the R enantiomer of the chiral solvent was used, the negative CPL peak was the one located at 544 nm and the positive peak was found at 549 nm. When the S enantiomer was used in place of the R, the CPL peaks occurred at the same wavelength, had the same intensity, but were of opposite sign.

The CPL spectra of other Tb(III) luminescent bands was also recorded, corresponding to the $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_6$, $^7\mathrm{F}_4$, and $^7\mathrm{F}_3$ transitions, but the CPL of these was at least an order of magnitude weaker than the CPL associated with the $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_5$ emission. An attempt to compare the CPL of the $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_6$ emission with the induced circular dichroism (CD) of the corresponding $^7\mathrm{F}_6 \rightarrow {}^5\mathrm{D}_4$ proved unsuccessful owing to the extremely low magnitude of optical activity found with both methods. CD measurements were not pursued further since the low signal-to-noise ratios obtained precluded effective