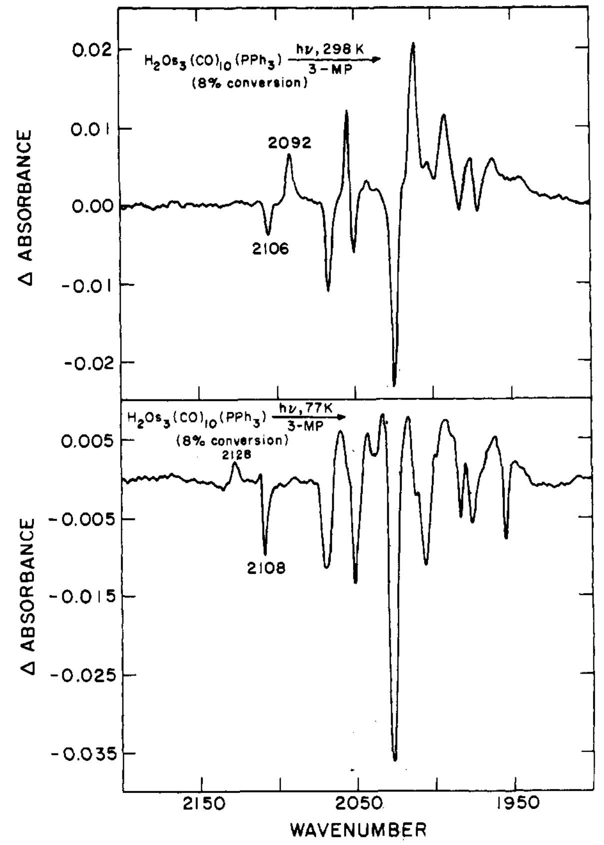

Figure 3. Comparison of difference spectra upon near-UV irradiation at 8% consumption of starting 1 mM $H_2Os_3(CO)_{10}(PPh_3)$ in 3-methylpentane at 298 and 77 K. Note that at 298 K $H_2Os_3(CO)_9(PPh_3)$ is formed (2092 cm^{-1}) whereas nearly none is detected at 77 K. Further irradiation at 77 K does produce $H_2Os_3(CO)_9(PPh_3)$ as for $H_2Os_3(CO)_{10}L$ shown in Figures 1 and 2.

is apparently not efficient, since we do not find release of Os species into solution from the irradiation of $[SiO_2]$–$L'Os_3(CO)_{10}H_2$. Interestingly, the low-temperature photochemistry of $H_2O_3(CO)_{10}L$ departs from the low-temperature photochemistry of $Mn_2(CO)_{10}$[3] and $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$[4,5] that do lose CO upon photoexcitation in rigid media but give metal–metal bond cleavage upon photoexcitation in fluid solution.

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Registry No. $H_2Os_3(CO)_{10}(PPh_3)$, 56398-26-6; $H_2Os_3(CO)_{10}(PPh_2Et)$, 78885-55-9; $H_2Os_3(CO)_9(PPh_3)$, 88510-52-5; $H_2Os_3(CO)_9(PPh_2Et)$, 75835-64-2; $H_2Os_3(CO)_9(PPh_2CH_2CH_2Si(OEt)_3)$, 88510-53-6; $H_2Os_3(CO)_{10}(PPh_2CH_2CH_2Si(OEt)_3)$, 88510-54-7; SiO_2, 7631-86-9; CO, 630-08-0.

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σ- and π-Acidity of $As(OTeF_5)_3$

Sir:

We have been exploring the use of $P(OTeF_5)_3$[1] and $As(OTeF_5)_3$[2,3] as extremely bulky substitutes for carbon monoxide in metal complexes. The pentafluoroorthotellurate $(OTeF_5)$[4] group has been substituted for fluorine or chlorine in a wide variety of main-group and high-valent transition-metal compounds.[5–7] By using various physicochemical criteria, including molecular structures (group site preferences),[8,9] NMR chemical shifts,[9–11] Mössbauer isomer shifts,[11] chemical reactivities,[12] and the thermal stabilities[13] of some main-group $OTeF_5$ derivatives, it has been repeatedly demonstrated that the electronegativity of $OTeF_5$ and fluorine are practically equal. This suggests the electronic similarity $P(OTeF_5)_3$ and $As(OTeF_5)_3 \sim PF_3$, $AsF_3 \sim CO$. Herein we report that $As(OTeF_5)_3$ behaves chemically like AsF_3 in its ability to form adducts with simple Lewis bases (σ-acidity) and to form complexes with low-valent transition metals (π-acidity). The occurence of both σ- and π-acidity in the same molecular species is rare.

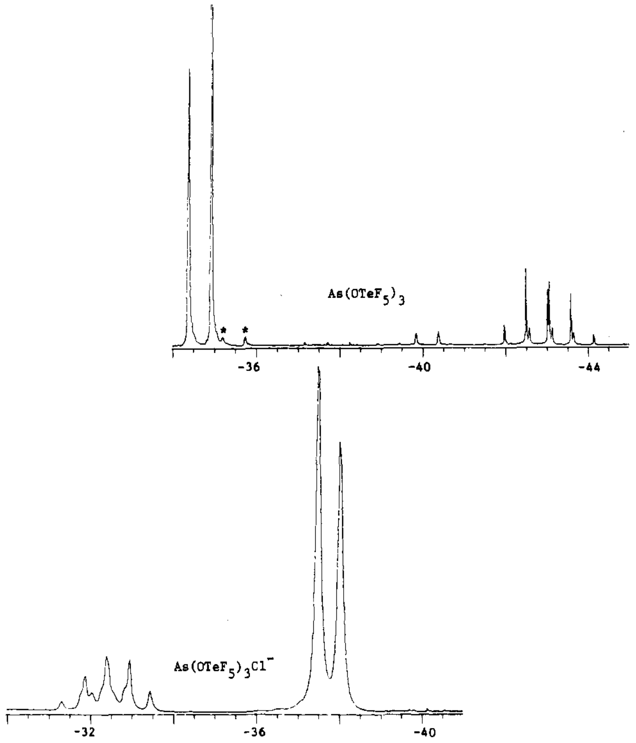

Figure 1. ^{19}F NMR spectra (338.8 MHz, 22 °C) of $As(OTeF_5)_3$ (upper trace) and $P(n\text{-}Bu)_4{}^+As(OTeF_5)_3Cl^-$ (lower trace). Both samples were 0.10 M in 50:50 CH_2Cl_2/CD_2Cl_2. Chemical shifts (ppm) are upfield of internal $CFCl_3$. Only half of the ^{125}Te satellites are visible in the upper trace. The two peaks marked with asterisks are due to an unidentified impurity.

The slightly volatile liquid $As(OTeF_5)_3$ was prepared by a literature procedure.[3] The ^{19}F NMR spectrum of this compound in CH_2Cl_2, shown in Figure 1 (top), is an AB_4X pattern

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[1] Lentz, D.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1983**, *502*, 83–8.
[2] Sladky, F.; Kropshofer, H. *J. Chem. Soc., Chem. Commun.* **1973**, 600–1.
[3] Seppelt, K. *Chem. Ber.* **1977**, *110*, 1470–6.
[4] We suggest the abbreviations teflate and teflic acid in place of the correct nomenclature pentafluoroorthotellurate and pentafluoroorthotelluric acid ($HOTeF_5$), respectively. The latter compound is the parent from which all teflates are prepared.[5,6]
[5] Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 877–88.
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[8] Seppelt, K.; Lentz, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 355.
[9] Lentz, D.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1980**, *460*, 5–16.
[10] Sladky, F.; Kropshofer, H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 195.
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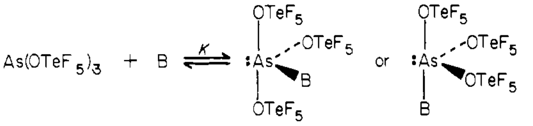
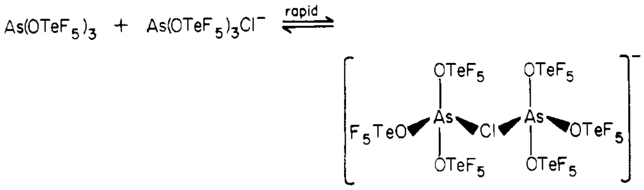
[12] (a) Sladky, F.; Kropshofer, H.; Leitzke, O. *J. Chem. Soc., Chem. Commun.* **1973**, 134–5. (b) Kropshofer, H.; Leitzke, O.; Peringer, P.; Sladky, F. *Chem. Ber.* **1981**, *114*, 2644–8.
[13] (a) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1559–70. (b) Seppelt, K.; Nothe, D. *Inorg. Chem.* **1973**, *12*, 2727–30. (c) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 356. (d) Lentz, D.; Seppelt, K. *Ibid.* **1979**, *18*, 66.

typical of $OTeF_5$ derivatives[14,15] and is in reasonable agreement with the data reported for this compound.[16]

The Lewis acidity of AsF_3 is limited to isolable adducts formed with alkali metal fluorides.[17] The AsF_4^- anion (local C_{2v} symmetry) has been structurally characterized in KAs_2F_7.[18] Using ^{19}F NMR spectroscopy, we have found that $As(OTeF_5)_3$ forms adducts with Lewis bases such as CH_3CN, Cl^-, and $OTeF_5^-$:[19–21]



The equilibrium constant, *K*, is large for B = Cl^- and $OTeF_5^-$ and is ~0.07 M^{-1} for B = CH_3CN. The equilibrium shown above is slowly maintained on the ^{19}F NMR time scale for B = CH_3CN and $OTeF_5^-$, as evidenced by sharp (line widths ~15 Hz) AB_4 resonances due to free $As(OTeF_5)_3$ and free (excess) $OTeF_5^-$, respectively, in these experiments. The AB_4 resonances due to $As(OTeF_5)_3(CH_3CN)$ and $As(OTeF_5)_4^-$, on the other hand, are considerably broader, most probably because of intramolecular exchange (pseudorotation of the axial and equatorial $OTeF_5$ groups in these adducts) that is insufficiently rapid to yield fast-exchange limit spectra.[22] Similarly, the AB_4 spectrum of $As(OTeF_5)_3Cl^-$ (see Figure 1 (bottom)) is also broad (line widths ~45 Hz at 22 °C) and broadens further as the temperature is lowered. However, a mixture of $As(OTeF_5)_3$ and $As(OTeF_5)_3Cl^-$ (~50:50) exhibits a sharp ^{19}F NMR spectrum (line width ~15 Hz):[23] the $OTeF_5$ groups of the two species are rapidly interconverting. While it is possible that the equilibrium shown above is faster for B = Cl^- than for B = CH_3CN and $OTeF_5^-$, we suggest the following exchange mechanism, which has no parallel for $As(OTeF_5)_3(CH_3CN)$ or $As(OTeF_5)_4^-$ because the $OTeF_5$ group has never been observed to bridge two elements:[5–7]



This type of intermolecular halogen exchange is not unexpected and has been suggested for species such as TeF_4,[24] SeF_4,[24] and $As_2F_3(SO_3F)_3$[25] and for BF_3/SF_4[26] and AsF_3/SbF_5[17] mixtures.

We have also found that the compounds $As(OTeF_5)_3$ and AsF_3 exhibit parallel chemical behavior *in addition to* their Lewis acidity: both can function as π-acids with low-valent transition metals. In the series of compounds $CpMn(CO)_3$, $CpMn(CO)_2(PF_3)$, and $CpMn(CO)_2(AsF_3)$, it was shown that AsF_3 is a stronger π-acid than PF_3.[27] Addition of $As(OTeF_5)_3$ or PF_3 to $W(CO)_5(THF)$ in THF solvent produces new infrared spectra with the concomitant disappearance of the $W(CO)_5(THF)$ spectrum (cm^{-1}):[28] $W(CO)_5(As(OTeF_5)_3)$ 2107 (A_1, w), 2004 (A_1, m), 1975 (E, s); $W(CO)_5(PF_3)$ 2101 (A_1, w), ~2005 (A_1, sh), 1975 (E, s). While detailed infrared studies of σ-donor vs. π-acceptor properties of ligands L are not complete for $W(CO)_5L$, our data clearly show that the π-acidity of $As(OTeF_5)_3$ and PF_3 are at least approximately equal.

The reactivity of a given metal complex is strongly dependent on the electronic and steric properties of its array of ligands. Frequently the two types of effects are inseparable, but it is well recognized that steric properties can be as important or more important than electronic properties in some cases.[29] Despite all of the elegant work that has been done with bulky trialkyl- and triarylphosphines and trialkyl and triaryl phosphites, the very recent synthesis of $Fe(CO)_4[P(OC(CF_3)_2CN)_3]$[30] is the only other literature report of a metal complex with a bulky *π-acid* phosphine or arsine. We are continuing to study the σ- and π-acidity of $As(OTeF_5)_3$ and $P(OTeF_5)_3$.

Acknowledgment is made to the Research Corp. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We thank Professor K. Seppelt for helpful comments concerning the synthesis of $HOTeF_5$, Professors D. E. Leyden and J. R. Norton for the use of their IR spectrometers, and C. E. Bronniman for recording the ^{19}F NMR spectra, which were obtained in the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE-8208821.

Registry No. $As(OTeF_5)_3(CH_3CN)$, 88548-68-9; $As(OTeF_5)_4^-$, 88548-69-0; $As(OTeF_5)_3Cl^-$, 88548-70-3; $W(CO)_5(As(OTcF_5)_3)$, 88548-71-4; $W(CO)_5(THF)$, 36477-75-5; $W(CO)_5(PF_3)$, 18461-47-7; $As(OTeF_5)_3$, 50652-21-6.

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(16) ^{19}F NMR (338.8 MHz, CH_2Cl_2 ($CFCl_3$ internal standard), 22 °C): AB_4X pattern (X = ^{125}Te, 7.0% NA, $I = {}^1/_2$) δ_A −43.3, δ_B −34.8 (J_{AB} = 180 Hz, J_{AX} = 3609 Hz, J_{BX} = 3690 Hz); lit.[14] (neat $CFCl_3$) δ_A −47.6, δ_B −37.5 (J_{AB} = 193 Hz, J_{AX} = 3568 Hz, J_{BX} = 3643 Hz); lit.[15] (solvent unspecified) δ_A −45.2, δ_B −36.1 (J_{AB} = 178 Hz). The ^{19}F chemical shifts of other teflates (including $HOTeF_5$, $B(OTeF_5)_3$, $CH_3CN{\cdot}B(OTeF_5)_3$, and $Hg(OTeF_5)_2$) in CH_2Cl_2 ($CFCl_3$ internal standard) are consistently a few ppm downfield of those reported[14] for the same compounds in neat $CFCl_3$: Abney, K. D.; Strauss, S. H., unpublished data, 1983.

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(19) Cl^- and $OTeF_5^-$ were added as $P(n\text{-}Bu)_4^+Cl^-$ and $PPN^+OTeF_5^-$, respectively.

(20) Electronegativity considerations alone would favor the first structure shown for B = CH_3CN and Cl^-.[21] However, note that matrix-isolated PF_3Cl^- probably has an axial chlorine: Wermer, P.; Ault, B. S. *Inorg. Chem.* **1981**, *20*, 970–3.

(21) Burdett, J. "Molecular Shapes"; Wiley-Interscience: New York, 1980; pp 105–8.

(22) The compound $Te(OTeF_5)_4$, which is probably isostructural with $As(OTeF_5)_4^-$, also undergoes rapid intramolecular exchange at room temperature: Lentz, D.; Pritzkow, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1926–31. See also ref 11.

(23) The two expected sets of AB_4 resonances are exchange averaged to yield a single resonance: the average δ_A and δ_B are apparently accidentally isochronous.

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(29) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–65. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–48. (c) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 10–2.

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Redox Behavior of Fe_4S_4 Clusters Surrounded by Hydrophobic Groups, $[Fe_4S_4(SC_6H_4R\text{-}p)_4]^{2-}$ (R = $n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$, and $n\text{-}C_{12}H_{25}$), in Aqueous Micellar Solutions

Sir:

Iron–sulfur proteins such as 4-Fe ferredoxins function as electron carriers in metabolism, and the active sites are known to be embedded in a hydrophobic environment of proteins.[1]

0020-1669/84/1323-0516$01.50/0