Both the porphyrin and the TMTAA ligand systems are tetradentate N_4-macrocycles that coordinate in the form of dianions. While the porphyrin dianion is a planar 18π-electron aromatic species, TMTAA is a 16π-electron antiaromatic dianion that can significantly deviate from planarity by rotation about the N-C bonds of the *o*-phenylenediamine portion of the macrocycle.[14] Close parallels between the organometallic chemistry of $(Rh(TMTAA))_2$ and $(Rh(Por))_2$ indicate that the conjugation and planarity of the porphyrin system are not essential features for the unusual reactivity that occurs at the rhodium center. The observed reaction of Rh(TMTAA)(py)(H) in pyridine with CO to produce a metallo formyl complex further extends the scope of complexes capable of this type of reaction to include six-coordinate rhodium(III) hydride species. The general reaction of a metal hydride with CO to produce observable concentrations of an η^1-carbon-bonded formyl complex is rare because of the thermodynamic requirement that the (M-H)-(M-C) bond energies must be relatively small (<10 kcal).[10,15] Accumulating evidence suggests that a large class of rhodium(III) hydride complexes may fulfill this thermodynamic criterion and could be effective in producing the initial steps in the hydrogenation of carbon monoxide.

Acknowledgment. This research was supported by the National Science Foundation and the Office of Basic Energy Sciences, DOE Grant No. DE-AC02-84ER-13133.

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Synthesis of Chelating Ditelluroether Ligands, $RTeCH_2CH_2CH_2TeR$ (R = Me, Ph)

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Received September 3, 1986

Summary: RTeLi (R = Me, Ph), prepared in situ in tetrahydrofuran from RLi and Te, react at low temperatures with 1,3-dihalopropanes, $X(CH_2)_3X$ (X = Cl, Br), to give high yields of $RTe(CH_2)_3TeR$. At ambient or higher temperatures these reactions yield mainly R_2Te_2. The $RTeCH_2TeR$ are made analogously, but 1,2-dichloroethane gave only R_2Te_2.

Despite the recent interest in organotellurium chemistry and its applications in synthesis,[1] nuclear medicine,[2] photography,[3] and new conducting materials,[4] the coordination chemistry of tellurium ligands remains underdeveloped in comparison with the selenium and sulfur analogues.[5] We were interested in extending our recent studies[6] on diselenoether complexes of the platinum metals and ^{77}Se NMR spectroscopy to the tellurium analogues. From the coordination chemists viewpoint, ligands with two- or three-carbon backbones leading to stable five- or six-membered chelate rings are preferable, but for tellurium all attempts to prepare $RTe(CH_2)_nTeR$ (n = 2, 3) are reported to have failed. In particular reaction of RTeM (M = alkali metal) with $X(CH_2)_nX$ (X = Cl, Br; n = 2, 3) at room temperature or above gave either R_2Te_2 + olefin or telluronium salts $R\overline{Te(C}H_2)_nX$.[7]

We have found that RTeLi (R = Me, Ph) are very conveniently obtained by an analogous method to that described for MeSeLi,[6] essentially adding RLi to a frozen mixture of tetrahydrofuran (THF) and elemental tellurium and allowing the mixture to warm to room temperature. If 1,3-dichloropropane is subsequently added at room temperature or above, the product is R_2Te_2, consistent with literature reports. However, if the THF solution is refrozen (−196 °C), then treated with $1,3\text{-}Cl(CH_2)_3Cl$, and allowed to warm slowly, after hydrolysis, drying, and removal of the solvent in vacuo the $RTe(CH_2)_3TeR$ are obtained in high yield[8] (85%, R = Ph; 73%, R = Me) and acceptable purity. The products appear to be stable at ambient temperatures. Characterization was by ^{1}H, ^{13}C, and ^{125}Te NMR and mass spectra[9] and by the preparation of derivatives.[10] In particular the ^{125}Te NMR chemical shifts of δ +104 (R = Me) and +465 (R = Ph) should be compared with those for MeTe-*n*-Pr and PhTe-*n*-Pr (δ +95 and 460, respectively).[11]

Similar reactions of RTeLi with CH_2Cl_2 provide good yields of $RTeCH_2TeR$, which have been independently obtained recently from R_2Te_2 and CH_2N_2,[12] $\delta(^{125}Te)$ 212 (R = Me) and 583.5 (R = Ph) (lit.[12] δ 213.5 and 587.6, respectively), but 1,2-dichloroethane affords only R_2Te_2 and C_2H_4 even at low temperatures. The greatest tendency to elimination is also observed with 1,2-dichloroalkanes and the corresponding element of group VB (15[14]) (antimony), although the $R_2Sb(CH_2)_nSbR_2$ (n = 1, 3; R = Me, Ph) can be prepared.[13]

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[8] $PhTe(CH_2)_3TePh$. Under a dinitrogen atmosphere, dry tetrahydrofuran (100 cm^3) was distilled onto tellurium powder (12.8 g, 0.1 mol) and frozen (−196 °C). Phenyllithium (55.6 cm^3, 1.8 M, 0.1 mol) was syringed in and the mixture allowed to thaw. When all the Te had dissolved, the clear solution was refrozen (−196 °C) and 1,3-dibromopropane (5.1 cm^3, 0.05 mol) added. The mixture was allowed to warm to room temperature and hydrolyzed (saturated aqueous NaCl solution), the organic phase separated and dried ($MgSO_4$), and the solvent removed in vacuo to leave a pale orange oil. $MeTe(CH_2)_3TeMe$ was made similarly from MeLi.

[9] $PhTe(CH_2)_3TePh$: ^{1}H NMR 2.2 (q, 2 H), 2.85 (t, 4 H), 6.9–7.8 ppm (m, 10 H); $^{13}C\{^1H\}$ NMR 138.2, 128.9, 127.3, 111.7, 33.2, 10.5 ppm ($^1J_{Te-C}$ = 158 Hz); $^{125}Te\{^1H\}$ NMR +465 ppm; mass spectrum (only ^{130}Te peak quoted), m/z 456 (M), 414 (M − $(CH_2)_3$), 379 (M − Ph), 337 ($PhTe_2$). $MeTe(CH_2)_3TeMe$: ^{1}H NMR 1.85 (s, 6 H), 2.05 (q, 2 H), 2.6 ppm (t, 4 H); $^{13}C\{^1H\}$ NMR 33.6, 5.2 ($^1J_{Te-C}$ = 153 Hz), −23.3 ppm ($^1J_{Te-C}$ = 162 Hz); $^{125}Te\{^1H\}$ NMR + 104 ppm. All in $CDCl_3$ relative to Me_4Si (^{1}H, ^{13}C) or external neat $TeMe_2$ (^{125}Te).

[10] Dimethiodides were prepared by stirring the ligand with MeI in acetone. $IPhMeTe(CH_2)_3TeMePhI$: $^{125}Te\{^1H\}$ NMR +609.7, +610.3 ppm. Anal. Calcd for $C_{17}H_{22}I_2Te_2$: C, 27.8; H, 3.0. Found: C, 28.3; H, 3.1. $IMe_2Te(CH_2)_3TeMe_2I$: $^{125}Te\{^1H\}$ +494 ppm. Anal. Calcd for $C_7H_{18}I_2Te_2$: C, 13.7; H, 2.9. Found: C, 13.5; H, 3.0.

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[14] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

0276-7333/87/2306-0206$01.50/0

The coordination chemistry of these ditelluroether ligands will be reported elsewhere in due course.

Acknowledgment. We thank the SERC for support (E.G.H. and T.K.) and Mrs. J. M. Street for the ^{13}C NMR spectra.

Reaction of a Terminal Phosphinidene Complex with a Carbene Complex. Synthesis of a Phosphorus–Carbon Double Bond through Phosphinidene–Carbene Coupling

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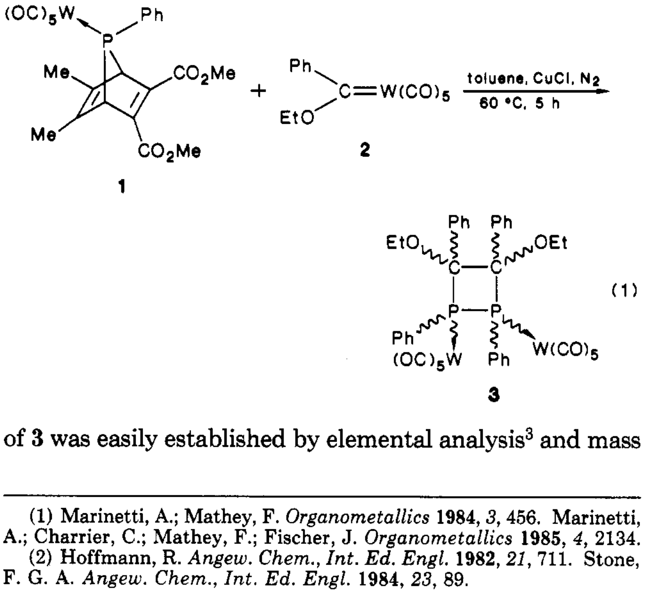
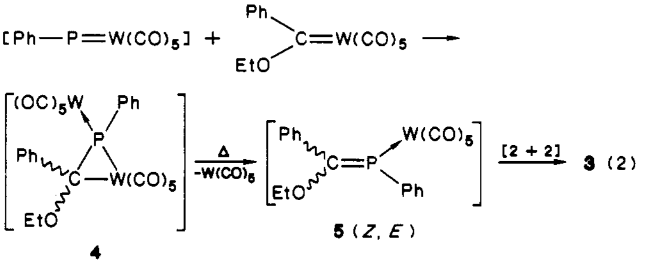
Summary: The reaction of (phenylethoxycarbene)pentacarbonyltungsten with transient (phenylphosphinidene)pentacarbonyltungsten gives (2-ethoxy-1,2-diphenylphosphaethylene)pentacarbonyltungsten. This phosphaalkene complex spontaneously dimerizes to form the corresponding 1,2-diphosphetane complex. This dimerization is reversible upon heating, and the phosphaalkene complex can be trapped as [4 + 2] cycloadducts by 2,3-dimethylbutadiene or cyclopentadiene.

We have recently shown that terminal phosphinidene complexes as generated by thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene complexes readily react with olefins to give the corresponding phosphirane complexes.[1] Since the $M(CO)_5$ groups (M = Cr, Mo, W) are isolobal with methylene,[2] it seemed possible to mimic this type of cycloadditions by using carbene complexes $R_2C{=}M(CO)_5$ in lieu of olefins in order to obtain, at least transiently, carbon–phosphorus–transition-metal three-membered heterocycles. We describe here our first attempt in this direction. The reaction of equimolar amounts of the 7-phosphanorbornadiene complex **1** with the carbene complex **2** in the presence of catalytic quantities of CuCl affords the 1,2-diphosphetane complex **3**[3] in ca 56% yield (eq 1). The empirical formula of **3** was easily established by elemental analysis[3] and mass spectrometry (EI, 70 eV, ^{184}W): m/z (relative intensity) 566 (M/2, 74), 510 (M/2 - 2CO, 47), 481 (M/2 - 3CO - H, 100). That the compound is an unsymmetrical dimer with a P–P bond was shown by its ^{31}P NMR spectrum: AB system, δ -80.06 and -71.10 in $CDCl_3$ (positive for downfield shifts from external 85% H_3PO_4), $^1J(P–P) = 97.7$ Hz. The ^1H and ^{13}C NMR spectra[3] confirmed the proposed formulation. The copper chloride serves to lower the decomposition temperature of **1** from ca. 110 to 50-60 °C.[1] This is necessary in view of the limited thermal stability of **2**. However, since CuCl does not interfere with the condensation of terminal phosphinidene complexes with olefins, it seems logical to assume that the same holds true in this case. Thus, the most logical mechanism explaining the formation of **3** is that depicted in eq 2.



3



The initial condensation would yield a three-membered ring such as **4** which is analogous to some already known σ,π-complexes of phosphaalkenes.[4] Then, **4** would spontaneously lose the π-bonded $W(CO)_5$ group[5] to give a mixture of the corresponding *Z* and *E* phosphaalkene σ-complexes **5**. The [2 + 2] dimerization of **5** would ultimately lead to **3**.[6]

Another phosphinidene–carbene coupling has been recently described,[7] but in the final product the formal P=C double bond thus formed is incorporated in a cluster and has completely lost its π-bond reactivity. This is not the case here. As suggested by the mass spectral data, the [2 + 2] dimerization leading to **3** is easily reversible upon heating and **3** can be used as a generator of P=C double bonded species. Indeed, the reactions of **3** with 2,3-dimethylbutadiene and cyclopentadiene in sealed tubes at ca. 130 °C in toluene afford the [4 + 2] cycloadducts **6**[8]

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[3] Compound **3** was purified by chromatography on Florisil (eluent pentane/CH_2Cl_2, 5/1). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.34 (s, Me), 60.98 (s, OCH_2), 65.61 (d, $^1J(C–P) = 11$ Hz, O–C–P), 195.38 (cis CO). IR (pentane): ν(CO) 2075 (m), 1955 (vs) cm^{-1}. Anal. Calcd for $C_{40}H_{30}O_{12}P_2W_2$: C, 42.44; H, 2.65; P, 5.48; W, 32.49. Found: C, 42.23; H, 2.65; P, 5.2; W, 33.0.

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[5] Similar losses have been described in the literature; for example, (PhP=PPh) $[Cr(CO)_5]_3$ loses its π-bonded $Cr(CO)_5$ upon heating to give $[Ph–\ddot{P}\rightarrow Cr(CO)_5]_2$: Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 977.

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[7] Williams, G. D.; Geoffroy, G. L.; Whittle, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 729.

[8] Compounds **6a,b** were purified by chromatography on silica gel at -10 °C (eluent pentane/CH_2Cl_2, 8/1). ^{31}P NMR ($CDCl_3$): δ +5.4 and +7.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.32 (s, OCH_2CH_3), 20.17 (s, Me), 21.53 (d, $^3J(C–P) = 8.5$ Hz, Me), 33.32 (d, $^1J(C–P) = 24.4$ Hz, CH_2P), 40.80 (d, $^2J(C–P) = 3.7$ Hz, CH_2), 58.22 and 58.76 (2s, OCH_2), 79.85 (d, $^1J(C–P) = 39$ Hz, C–P), 123.01 (d, $J(C–P) = 3.7$ Hz, =CMe), 197.14 (d, $^2J(C–P) = 7.3$ Hz, cis CO). MS (EI, 70 eV, ^{184}W): m/z (relative intensity) 648 (M, 87), 508 (M - 5CO, 100). IR (CH_2Cl_2): ν(CO) 2075 (m), 1942 (vs) cm^{-1}. Anal. Calcd for $C_{26}H_{25}O_6PW$: C, 48.16; H, 3.86; O, 14.82; P, 4.78; W, 28.38. Found: C, 47.92; H, 3.99; O, 15.11; P, 4.53; W, 28.30. One isomer ($\delta(^{31}P)$ +5.4) has been obtained in the pure state by slow recrystallization from CH_2Cl_2/pentane (4/1): mp 177–179 °C; ^1H NMR ($CDCl_3$): δ 1.25 (t, $^3J(H–H) = 6.8$ Hz, 3 H, OCH_2CH_3), 1.78 (s br, 3 H, Me), 1.94 (s br, 3 H, Me), 2.72 (m, 2 H, CH_2P), 2.84 (m, 2 H, CH_2), 3.30 (q, 2 H, OCH_2).

0276-7333/87/2306-0207$01.50/0