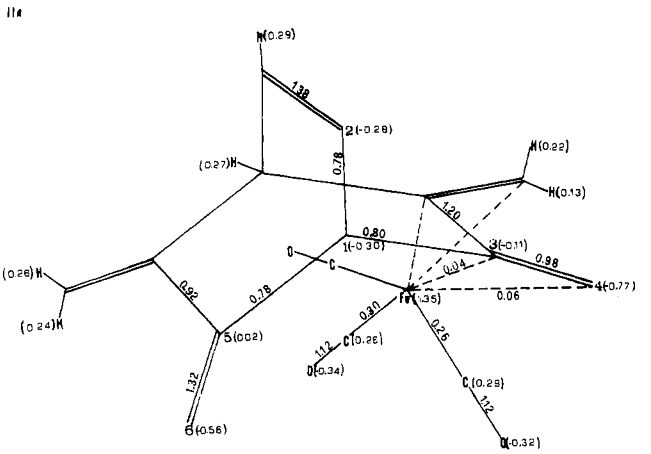

Figure 9. Ab initio gross atomic charges (in parentheses) and overlap populations of IIn complex obtained by Mulliken's population analysis.

note that such behavior is exhibited by those MOs whose corresponding PE bands were not in agreement with the expectations based on Worley's model (see previous paragraph). Since this mixing is present only for the π_1 MOs of the endo isomer, we may suggest some active role of the $Fe(CO)_3$ group in the endo position. The reason why such a mixing is evident only in the π_1 and not in the π_2 orbitals could be ascribed to the larger localization of the π_1 orbitals on the internal C_3 and C_5 atoms of the two butadiene moieties (which are close to the $Fe(CO)_3$ group).

The outermost occupied levels of the two isomers are compared in Figure 7. Remarkable differences are found although the gross features of $Fe(CO)_3$–butadiene bonding is similar in both cases. These differences do not result in significant differences in the net atomic charges and total overlap populations of the two complexes (see Figures 8 and 9). Hence we interpret the aforesaid differences in the eigenvalues (Figure 7) as reflecting minor long-range electrostatic effects. In fact, assuming the $Fe(CO)_3$ group as a positively charged group, we can interpret qualitatively the stabilization of $\pi_2{}^f$ and the destabilization of π_b[27] on going from IIx to IIn as an electrostatic energy shift, visible only for those MOs not directly involved into the bonding with the $Fe(CO)_3$ group.

As a final consideration derived from these theoretical results, we would like to comment on the model used to interpret the complexation shifts of the PE bands assigned to ligand-based MOs. Worley et al.[18] derived such complexation shifts comparying the PE spectra of the free and complexed ligands; caution is needed in extrapolating those shifts and their significance to molecules containing two ligating groups (one free and one complexed). In fact, the present theoretical results show that to assign band D in the PE spectrum of IIn to the $\pi_1{}^f$ MO is an unaccettable oversimplification due to the mentioned mixing between the $\pi_1{}^c$ and $\pi_1{}^f$ MOs.

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Registry No. Ia, 95017-43-9; IIx, 72983-28-9; IIn, 72984-40-8; IIIx, 72924-38-0; IIIn, 75597-78-3; IVnx, 63945-85-7; IVxx, 63976-22-7; Vnx, 75528-84-6; VInx, 75528-83-5; VIxn, 75597-80-7; VIxx, 75597-79-4; VIIx, 71520-86-0; $Fe(CO)_3$–butadiene, 12078-32-9.

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[27] According to the results of the Mulliken's population analysis, no direct interaction of π_b with the $Fe(CO)_3$ groups is to be claimed.

Synthesis of Five- and Six-Membered Ylide–Chelate Complexes by the Reaction of Pentacarbonyl(dimethyloxosulfonium methylide)chromium(0) with Bis(arsines) of the Type $(R_2As)_2X$ (X = C=PPh$_3$, NMe, O, S) and 1,2-Ethylenebis(phosphines) and -bis(arsines)[1]

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The reaction of $(R_2As)_2X$ (X = C=PPh$_3$, NMe, O; R = Me, Ph) with $Cr(CO)_5[CH_2S(O)Me_2]$ in toluene at 45 °C results in the formation of a series of arsonium ylide–chelate complexes $(CO)_4\overline{CrCH_2AsR_2XAs}R_2$). The complex derived from $(Ph_2As)_2O$ is converted into $(CO)_4\overline{CrCH_2As(Ph)_2SAs}Ph_2$ by treatment with gaseous hydrogen sulfide. The reactions of $R^1{}_2E^1CH_2CH_2E^2R^2{}_2$ (E = P, As; R = Me, Ph) with $Cr(CO)_5[CH_2S(O)Me_2]$ afford novel six-membered ylide–chelate complexes of the type $(CO)_4\overline{CrCH_2E^1R^1{}_2(CH_2)_2E^2}R^2{}_2$ as well as the known five-membered chelates $(CO)_4\overline{CrE^1R^1{}_2(CH_2)_2E^2}R^2{}_2$. The novel coordination compounds have been characterized by elemental analysis and infrared, proton, and phosphorus NMR spectroscopy.

Introduction

The work reported here is a result of our continuing interest in the synthesis and reactivity of transition metal–sulfur ylide complexes.[2] Thus recently we reported the preparation of five-membered metallaheterocycles of the type $(CO)_4\overline{CrCH_2ER_2CH_2E}R_2$ by treatment of the sulfur ylide complex $Cr(CO)_5[CH_2S(O)Me_2]$ (1) with methylenebis(phosphines) and $(Ph_2As)_2CH_2$ (2a) (eq 1).[3,4] These

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[1] Transition Metal Complexes of Unstable Ylides. 6. For part 5, see: Weber, L.; Wewers, D. *Chem. Ber.* 1985, *118*, 541.

[2] Weber, L. *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 516.

[3] Weber, L.; Wewers, D.; Meyer, W.; Boese, R. *Chem. Ber.* 1984, *117*, 732.

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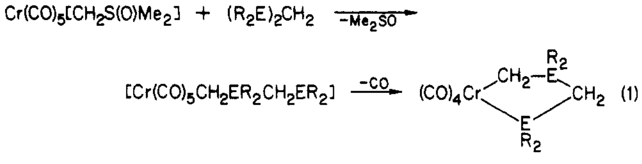
heterocycles can be considered as containing the unstable ylides $CH_2{=}ER_2CH_2ER_2$ as chelating ligands at the tetracarbonylchromium fragment.



$R_2E = Ph_2P, Me_2P, (Me_2N)_2P, Ph_2As$ (**3a**)

Compared to the large number of phosphonium ylide complexes[5] the coordination chemistry of arsonium ylides has attracted little attention.[6] This is to some extent due to the decreased stability of simple arsonium ylides.[7]

Thus it was of interest to extent the reaction of $Cr(CO)_5[CH_2S(O)Me_2]$ with $(Ph_2As)_2CH_2$ to other arsines. Especially interesting was the question as to whether functionalities other than methylene groups are tolerated between the two arsenic centers. Addressing this question we examined the reaction of **1** with $(Ph_2As)_2C{=}PPh_3$ (**2b**), $(Me_2As)_2NMe$ (**2c**), $(Ph_2As)_2O$ (**2d**), and $(Ph_2As)_2S$ (**2e**) as representative compounds containing an ylidic functionality, an imino group, and chalcogen atoms bridging the two arsenic atoms.

In the course of our studies we are also focussing on the question as to whether this ring closure reaction can also be realized with 1,2-ethylenebis(phosphines) and -bis(arsines). This would provide an entry into the rare class of chelate complexes featuring $\overline{MCH_2ER_2CH_2CH_2ER_2}$ metallaheterocycles. Here we also report on our results of **1** with the aforementioned bis(phosphines) and bis(arsines).

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The ^1H and ^{31}P NMR spectra were taken on a Varian XL 200 NMR spectrometer. Spectral standards were $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on Varian MAT 312 (EI) and Varian MAT 711 (FD) spectrometers. Elemental analyses were performed in the Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim, Germany, and in the Mikroanalytical Laboratory of the Universität Essen.

Materials. The arsines Ph_2AsCl,[8] $(Me_2As)_2NMe$,[9] $(Ph_2As)_2O$,[10] $(Ph_2As)_2S$,[11] $Ph_2As(CH_2)_2AsPh_2$,[12] the phosphines $Ph_2PCH_2CH_2PPh_2$[13] and $Me_2PCH_2CH_2PMe_2$,[14] the ylide $Ph_3P{=}CH_2$,[15] the sulfonium ylide complex $Cr(CO)_5[CH_2S(O)Me_2]$,[16] and the compound $(C_7H_8)Cr(CO)_4$[17] were prepared as described in the literature. $Ph_2AsCH_2CH_2PPh_2$ was purchased from Strem Chemicals. All solvents were rigorously dried with an appropriate drying agent and distilled prior to use.

Preparation of Compounds. Triphenylphosphonium Bis(diphenylarsino)methylide (2b). By analogy with the synthesis of $(Ph_2Sb)_2C{=}PPh_3$[18] a solution of 3.46 g (13.1 mmol) of chlorodiphenylarsine in 20 mL of toluene was added dropwise to a vigorously stirred toluene solution of 5.34 g (19.6 mmol) of triphenylphosphonium methylide at 70 °C. Stirring was continued for 3 h. The precipitate was filtered and washed with toluene (3 × 40 mL). Solvent was removed from the yellow filtrate in vacuo, and the yellow residue was redissolved in 20 mL of toluene. Precipitation of analytically pure **2b** was effected by the dropwise addition of 60 mL of pentane: mp 103 °C dec; yield 3.73 g (78%); IR (Nujol) 978 (ν(P=C) cm^{-1}; $^{31}P\{^1H\}$NMR (THF) δ 27.13. Anal. Calcd for $C_{43}H_{35}As_2P$ (732.6): C, 70.50; H, 4.82. Found: C, 70.14; H, 4.96; mol wt, 732 (MS, EI).

Reaction of 1 with Triphenylphosphonium Bis(diphenylarsino)methylide (2b). A mixture of 0.385 g (1.35 mmol) of **1** and 0.992 g (1.35 mmol) of **2b** was stirred in 45 mL of toluene at 45 °C for 24 h. A yellow precipitate was filtered, washed with 10 mL of pentane, and dried in vacuo: yield 0.568 g (46%) of pure **3b**; IR (Nujol) 1977 s, 1884 s, 1857 vs, 1844 s, 1807 vs (ν(CO)), 1443 m, 1097 m, 973 m, 790 m, 740 m, 692 m, 655 m cm^{-1}; ^1H NMR (C_5D_5N) δ 1.99 (s, 2 H, $CrCH_2$), 7.0–8.0 (m, 35 H, Ph); $^{31}P\{H\}$NMR (C_5D_5N) δ 22.61. Anal. Calcd for $C_{48}H_{37}As_2CrO_4P$ (910.6): C, 63.31; H, 4.10; Cr, 5.71. Found: C, 62.98; H, 4.10; Cr, 5.86; mol wt, 910 (MS, FD).

In the yellow mother liquor complex **4b** as well as a pentacarbonylchromium species was detected by means of IR spectroscopy. The isolation of these products, however, failed.

Reaction of 1 with Bis(dimethylarsino)methylamine (2c). A mixture of 0.604 g (2.12 mmol) of **1** and 0.508 g (2.12 mmol) of **2c** was stirred in 50 mL of toluene at 45 °C for 48 h. The filtered solution was evaporated to dryness, and the yellow residue was recrystallized from CH_2Cl_2/pentane to yield 0.290 g (33%) of **3c**: IR (Nujol) 1983 s, 1860 vs, 1812 vs (ν(CO)), 1092 m, 768 m, 690 m, 658 m, 647 m cm^{-1}; ^1H NMR (C_5D_5N) δ 0.83 (s, 2 H, $CrCH_2$), 1.51 (s, 6 H, Me_2As^{III}), 1.57 (s, 6 H, Me_2As^{V}), 2.76 (s, 3 H, NMe). Anal. Calcd for $C_{10}H_{17}As_2CrNO_4$ (417.1): C, 28.80; H, 4.11; Cr, 12.47; N, 3.36. Found: C, 28.75; H, 4.10; Cr, 12.27; N, 2.86; mol wt, 417 (MS, FD).

The yellow mother liquor contained **4c** and a pentacarbonyl complex, the isolation of which failed.

Reaction of 1 with Bis(diphenylarsino) Oxide (2d). The reaction of 2.529 g (8.90 mmol) of **1** with 4.221 (8.90 mmol) of **2d** was performed in 150 mL of toluene at 45 °C. After 24 h the yellow solution was filtered and the solvents were removed from the filtrate by evaporation in vacuo. The oily green yellowish residue was dissolved in CH_2Cl_2 (20 mL). A green oil separated on dropwise addition of 40 mL of pentane. The supernatant solution was decanted and chilled at −30 °C. After 24 h 2.64 g of crystalline yellow **3d** (46%) was collected by filtration: IR (Nujol) 1993 s, 1897 s, 1867 vs, 1832 vs (ν(CO)), 1435 m, 747 m, 737 m, 695 m, 677 m, 652 m, 634 m, 555 m, 485 m cm^{-1}; ^1H NMR (C_5D_5N) δ 2.05 (s, 2 H, $CrCH_2$), 7.0–8.0 (m, 20 H, Ph). Anal. Calcd for $C_{29}H_{22}As_2CrO_5$ (652.3): C, 53.40; H, 3.40; Cr, 7.97. Found: C, 53.83; H, 3.38; Cr, 7.99; mol wt, 652 (MS, FD).

The mother liquor was freed from solvent in vacuo. The yellow residue was chromatographed on silica (Silica 60, 0.063–0.200 mm, Merck) using CH_2Cl_2 as eluant. A yellow band eluted, from which 0.830 g (14%) of **5d** was isolated: IR (Nujol) 2070 (s), 1990 (s),

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1958 (vs), 1948 (vs), 1939 (vs), 1925 (vs) (ν(CO)) 1438 (m), 752 (m), 740 (m), 731 (m), 698 (m), 677 (m), 662 (m), 650 (m) cm^{-1}; ^{1}H NMR (C_5D_5N) δ 7.0–8.0 (m, Ph). Anal. Calcd for $C_{29}H_{20}As_2CrO_6$ (666.3): C, 52.28; H, 3.03; Cr, 7.80. Found: C, 52.10; H, 3.12; Cr, 7.82; mol wt, 666 (MS, FD).

Reaction of 1 with Bis(diphenylarsino) Sulfide (2e). A mixture of 0.284 g (1.00 mmol) of **1** with 0.490 g (1.00 mmol) of **2e** were reacted as described above. In the reaction mixture only the presence of **5e** was unambigously proven by IR spectral comparison.

Reaction of 3d with H_2S. Gaseous hydrogen sulfide was bubbled through a solution of 0.721 g (1.10 mmol) of **3d** in 35 mL of CH_2Cl_2. After 1 min the reaction was stopped and the brown-red solution evaporated to dryness. Orange-red **3e** was isolated from the residue by column chromatography on silica (Silica 60, 0.063–0.200 mm, Merck) with CH_2Cl_2 as eluant: yield 0.130 g (14%); IR (Nujol) 1997 s, 1883 vs, 1825 vs (ν(CO)), 1435 m, 738 m, 690 m, 672 m, 663 m, 597 m, 480 m, 465 m cm^{-1}; ^{1}H NMR (C_5D_5N) δ 2.57 (s, 2 H, $CrCH_2$), 7.0–8.0 (m, 20 H, Ph). Anal. Calcd for $C_{29}H_{22}As_2CrO_4S$ (668.4): C, 52.11; H, 3.31; Cr, 7.78; S, 4.80. Found: C, 52.09; H, 3.38; Cr, 7.99; S, 5.23; mol wt, 668 (MS, FD).

Preparation of Complexes $(CO)_4Cr[(R_2As)_2X]$ (4b–e) from Tetracarbonyl(norbornadiene)chromium and 2b–e. Tetracarbonyl[triphenylphosphonium bis(diphenylarsino)-methylide]chromium (4b). A solution of 0.198 g (0.77 mmol) of $(C_7H_8)Cr(CO)_4$ and 0.565 g (0.77 mmol) of **2b** was stirred in 60 mL of cyclohexane at 45 °C for 4 h. The yellow precipitate of **4b** was filtered, washed twice with 10 mL of hexane, and dried in vacuo: yield 0.526 g (76%); IR (Nujol) 1995 s, 1893 vs, 1872 vs, 1830 vs (ν(CO)), 1433 m, 1095 m, 1083 w, 1043 w, 1017 m, 1000 m, 765 w, 733 m, 693 m, 645 m cm^{-1}; ^{1}H NMR (C_5D_5N) δ 7.0–8.0 (m, 35 H, Ph); ^{31}P{H}NMR (C_5D_5N) δ 5.37. Anal. Calcd for $C_{47}H_{35}As_2CrO_4P$ (896.6): C, 62.96; H, 3.93; Cr, 5.80. Found: C, 62.64; H, 3.90; Cr, 6.08; mol wt, 896 (MS, FD).

Tetracarbonyl[bis(dimethylarsino)methylamine]chromium (4c). From the analogous reaction of 0.402 g (1.57 mmol) of $(C_7H_8)Cr(CO)_4$ and 0.375 g (1.57 mmol) of **2c** was obtained 0.377 g (60%) of yellow **4c**: IR (Nujol) 2010 s, 1937 s, 1898 vs, 1875 vs, 1847 vs (ν(CO)), 908 w, 867 w, 720 w, 682 m, 658 m, 648 m, 642 m, 488 w cm^{-1}; ^{1}H NMR (C_5D_5N) δ 1.46 (s, 12 H, Me_2As), 2.47 (s, 3 H, NMe). Anal. Calcd for $C_9H_{15}As_2CrNO_4$ (403.1): C, 26.82; H, 3.75; N, 3.48; Cr, 12.90. Found: C, 26.41; H, 3.76; N, 3.07; Cr, 12.90; mol wt, 403 (MS, FD).

Tetracarbonyl[bis(diphenylarsino) oxide]chromium (4d). Analogously 0.369 g (58%) of **4d** was prepared from 0.256 g (1.00 mmol) of $(C_7H_8)Cr(CO)_4$ and 0.474 g (1.00 mmol) of **2d**: IR (Nujol) 2025 s, 1920 vs, 1905 vs, 1887 vs (ν(CO)), 760 w, 748 m, 733 m, 692 m, 639 m cm^{-1}; ^{1}H NMR (C_5D_5N) δ 7.0–8.0 (m, 20 H, Ph). Anal. Calcd for $C_{28}H_{20}As_2CrO_5$ (638.3): C, 52.69; H, 3.40; Cr, 8.15. Found: C, 52.18; H, 3.24; Cr, 8.11; mol wt, 638 (MS, FD).

Tetracarbonyl[bis(diphenylarsino) sulfide]chromium (4e). Analogously 0.334 g (51%) of yellow **4e** was prepared by reaction of 0.256 g (1.00 mmol) of $(C_7H_8)Cr(CO)_4$ and 0.490 g (1.00 mmol) of **2e**: IR (Nujol) 2018 s, 1928 s, 1889 vs (ν(CO)), 745 m, 738 m, 697 m, 674 m, 642 s cm^{-1}; ^{1}H NMR (C_5D_5N) δ 7.0–8.0 (m, 20 H, Ph). Anal. Calcd for $C_{28}H_{20}As_2CrO_4S$ (654.4): C, 51.39; H, 3.08; Cr, 7.95; S, 4.90. Found: C, 50.51; H, 3.09; Cr, 7.99; S, 4.97; mol wt, 654 (MS, FD).

Preparation of Pentacarbonyl[bis(diphenylarsino) sulfide]chromium (5e). A solution of 0.286 g (1.30 mmol) of $Cr(CO)_6$ and 2 mL of (*Z*)-cyclooctene was irradiated in 100 mL of hexanes at 15 °C until CO evolution ceased. Then 0.490 g (1.00 mmol) of **2e** was added to the resulting yellow solution of $(CO)_5Cr(C_8H_{14})$, and the mixture was stirred for 4 days at 45 °C. The light yellow precipitate of **5e** was filtered, washed with 10 mL of hexanes, and dried in vacuo: yield 0.355 g (52%); IR (Nujol) 2065 m, 1987 w, 1950 s, 1937 s, 1928 s (ν(CO)), 733 m, 692 m, 678 m, 660 m, 652 m, 480 m, 470 m cm^{-1}; ^{1}H NMR (C_5D_5N) δ 7.0–8.0 (m, Ph). Anal. Calcd for $C_{29}H_{20}As_2CrO_5S$ (682.4): C, 51.04; H, 2.95; Cr, 7.62. Found: C, 50.66; H, 3.12; Cr, 7.72; mol wt, 682 (MS, FD).

Tetracarbonyl{[2-(diphenylphosphino)ethyl]diphenylphosphonium methylide-*α*-*C*,*ω*-*P*}chromium(0) (8a). A mixture of 0.408 g (1.44 mmol) of **1** and 0.463 g (1.44 mmol) of **7a** was stirred in 50 mL of toluene at 60 °C for 20 h and then filtered. All volatiles were removed in vacuo from the filtrate. The yellow residue was dissolved in 4 mL of CH_2Cl_2, then pentane was added until cloudiness persisted, and the mixture was then cooled in an ice bath to induce crystallization of **8a**. The product was collected, washed with cold pentane, and dried in vacuo to give 0.321 g (39%) of pure **8a**: IR (Nujol) 1982 s, 1872 s, 1857 vs (ν(CO)), 1438 m, 1260 w, 1160 w, 1126 w, 1103 m, 999 w, 932 w, 867 m, 857 w, 808 w, 742 m, 725 m, 711 m, 691 s, 667 m, 655 m, 648 m, 541 m, 517 w, 499 m, 490 w, 477 w cm^{-1}; ^{1}H NMR (C_5D_5N) δ 0.78 (dd, J = 12.3, 8.1 Hz, 2 H, $CrCH_2$), 2.72–2.97 (m, 4 H, CH_2CH_2), 7.26–8.00 (m, 20 H, Ph); ^{31}P{H} NMR (C_5D_5N) δ 31.68 (d, J = 5 Hz, P(V)), 53.00 (d, J = 5 Hz, P(III)); MS (EI, 70 eV, 150 °C), *m/e* 562 ($M^+ - CH_2$), 478 ($M^+ - 3CO - CH_2$), 464 ($M^+ - 4CO$), 450 ($M^+ - 4CO - CH_2$), 422 ($M^+ - 4CO - CH_2 - C_2H_4$), 398 ($Ph_2PCH_2CH_2PPh_2^+$), 262 ($PPh_3^+$), 252 ($Cr(MePPh_2)^+$), 200 ($MePPh_2^+$), 183 ($PC_{12}H_8^+$), 108 ($PPh^+$), 92 ($C_7H_8^+$), 78 ($C_6H_6^+$), 52 ($Cr^+$). Anal. Calcd for $C_{31}H_{26}CrO_4P_2$ (576.5): C, 64.59; H, 4.55; Cr, 9.02. Found: C, 64.33; H, 4.60; Cr, 9.12; mol wt, 602 (osmometrically in CH_2Cl_2).

Tetracarbonyl{[2-(dimethylphosphino)ethyl]dimethylphosphonium methylide-*α*-*C*,*ω*-*P*}chromium(0) (8b). A mixture of 2.643 g (9.30 mmol) of **1** and 1.396 g (9.30 mmol) of **7b** was stirred in 150 mL of toluene at 60 °C for 22 h. Filtration and evaporation to dryness yielded a yellow residue, which was recrystallized from CH_2Cl_2/ether mixtures: yield 0.630 g (21%) of pure yellow **8b**; IR (Nujol) 1977 s, 1875 vs, 1845 vs [ν(CO)], 1420 m, 1407 w, 1305 w, 1296 m, 1283 w, 1141 w, 1107 w, 948 s, 917 s, 902 w, 850 w, 813 w, 757 w, 737 m, 721 m, 706 m, 690 s, 657 s cm^{-1}; ^{1}H NMR (C_5D_5N) δ −0.20 (dd, J = 13.2, 8.6 Hz, 2 H, $CrCH_2$), 1.40 (d, J = 6.4 Hz, 6 H, Me_2P^{III}, 1.54 (d, J = 12.5 Hz, 6 H, Me_2P^V), 1.60–2.00 (m, 4 H, CH_2CH_2); ^{31}P{H} NMR (C_5D_5N) δ 31.41 (d, J = 18 Hz, P(V)), 22.81 (d, J = 18 Hz, P(III)); MS (EI, 70 eV, 150 °C), *m/e* 328 (M^+), 314 ($M^+ - CH_2$), 300 ($M^+ - CO$), 244 ($M^+ - 3CO$), 230 ($M^+ - 3CO - CH_2$), 216 ($M^+ - 4CO$), 202 ($M^+ - 4CO - CH_2$), 188 ($M^+ - 4CO - 2CH_2$), 174 ($M^+ - 4CO - 3CH_2$), 149 [$Me_2P(CH_2)_2P(Me){=}CH_2^+$], 128 ($CrPMe_3^+$), 113 ($CrPMe_2^+$), 76 ($PMe_3^+$), 52 ($Cr^+$). Anal. Calcd for $C_{11}H_{18}CrO_4P_2$ (328.2): C, 40.25; H, 5.53; Cr, 15.84. Found: C, 39.87; H, 5.88; Cr, 15.41.

Tetracarbonyl{[2-(diphenylarsino)ethyl]diphenylphosphonium methylide-*α*-*C*,*ω*-*As*}chromium(0) (8c). A mixture of 0.284 g (1.00 mmol) of **1** and 0.442 (1.00 mmol) of **7c** was allowed to react in 50 mL of toluene at 60 °C for 7 h. Stirring was continued at 20 °C for another 16 h. The mixture was filtered, and volatile material was removed in vacuo. Recrystallization of the yellow residue from CH_2Cl_2/hexanes at 0 °C gave 0.160 g (26%) of pure yellow **8c**: IR (Nujol) 1989 s, 1883 s, 1862 vs, 1811 vs [ν(CO)], 1439 w, 1435 w, 1376 m, 1307 w, 1260 w, 1120 w, 1104 m, 980 w, 930 w, 841 m, 747 w, 737 w, 710 w, 690 m, 658 w, 650 m, 606 w, 556 w, 509 w, 487 w cm^{-1}; ^{1}H NMR (C_5D_5N) δ 0.73 (d, J = 13.3 Hz, 2 H, $CrCH_2$), 2.69 (m, 2 H, PCH_2), 3.00 (m, 2 H, $AsCH_2$), 7.25–8.00 (m, 20 H, Ph); ^{31}P{H} NMR (C_5D_5N) δ 32.29; MS (EI, 70 eV, 150 °C), *m/e* 550 ($M^+ - 2CO - CH_2$), 538 ($M^+ - 2CO - C_2H_2$), 508 ($M^+ - 4CO$), 494 ($M^+ - 4CO - CH_2$), 458 ($M^+ - 3CO - C_6H_6$), 306 ($CrAs(Ph_2)CCH^+$), 280 ($CrCH_2P(Ph_2)Et^+$), 251 ($CrCH_2PPh_2^+$), 229 ($PMeEtPh_2^+$), 200 ($MePPh_2^+$), 183 ($PC_{12}H_8^+$), 152 ($AsPh^+$), 78 ($C_6H_6^+$), 52 (Cr^+). Anal. Calcd for $C_{31}H_{26}AsCrO_4P$ (620.4), C, 60.01; H, 4.22; Cr, 8.38. Found: C, 59.87; H, 4.33; Cr, 8.20; mol wt, 620 (MS, FD).

From the mother liquor 0.129 g (21%) of yellow **9c** could be obtained by slow addition of hexanes. This material proved to be identical with an authentic sample.[19]

Tetracarbonyl{[2-(diphenylarsino)ethyl]diphenylarsonium methylide-*α*-*C*,*ω*-*As*}chromium(0) (8d). As described above the reaction of 0.286 g (1.01 mmol) of **1** with 0.489 g (1.01 mmol) of **7d** yielded 0.128 g (20%) yellow **8d**: IR (Nujol) 1987 s, 1884 vs, 1858 vs, 1810 vs (ν(CO)), 1576 w, 1483 w, 1439 m, 1433 m, 1309 w, 1258 w, 1182 w, 1090 w, 1082 m, 1032 w, 998 w, 959 w, 916 w, 823 m, 783 m, 743 m, 735 m, 693 s, 667 w, 648 s, 616 m cm^{-1}; ^{1}H NMR (C_5D_5N) δ 1.12 (s, 2 H, $CrCH_2$), 2.74 (m, 2 H, CH_2As^{III}), 3.03 (m, 2 H, CH_2As^V); MS (EI, 70 eV, 150 °C), *m/e* 650 ($M - CH_2$), 622 ($M^+ - CH_2 - CO$), 594 ($M^+ - CH_2 - 2CO$), 566 ($M^+ - CH_2 - 3CO$), 538 ($M^+ - CH_2 - 4CO$), 510 ($M^+ - CH_2 - 4CO - C_2H_4$), 486 [$(Ph_2AsCH_2)_2^+$], 458 ($Ph_2AsAsPh_2^+$), 229

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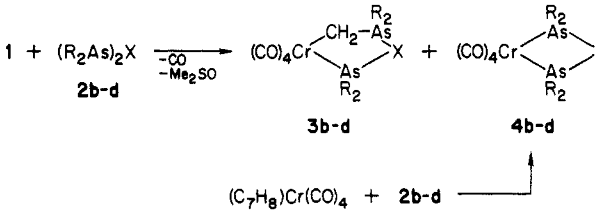
[19] Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* 1973, 347.

(Ph_2As^+), 152 $(PhAs^+)$, 52 (Cr^+). Anal. Calcd for $C_{31}H_{26}As_2CrO_4$ (664.4): C, 56.04; H, 3.94; Cr, 7.83. Found: C, 55.25; H, 3.98; Cr, 7.42.

From the mother liquor 0.060 g (9%) of **9d** identical with an authentic sample[20] was isolated by fractional crystallization from CH_2Cl_2/hexanes.

Results and Discussion

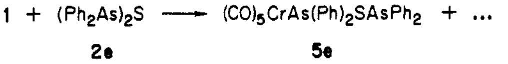
(A) Five-Membered Arsonium Ylide–Chelate Complexes. Yellow, air-stable chelate complexes **3b–d** were obtained by the reaction of pentacarbonyl(dimethyloxosulfonium methylide)chromium (**1**) with the bis(arsines) **2b–d** in toluene at 45 °C. In addition, the bis(arsine) tetracarbonylchromium complexes **4b–d** were formed but their attempted isolation failed. The latter compounds were identified by comparison of their infrared spectra with those of authentic samples, which were prepared from tetracarbonyl(norbornadiene)chromium and **2b–d** (eq 2).



(2)

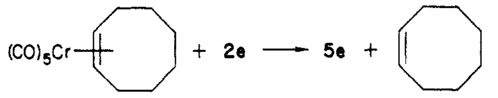
b, R = Ph, X = C=PPh$_3$; c, R = Me, X = NMe; d, R = Ph, X = O

$(CO)_5Cr(Ph_2AsOAsPh_2)$ also was formed in the reaction of **1** with **2d** and was isolated by column chromatography on silica. Complex **1** could not be transformed to metallacycle **3e** by treatment with bis(diphenylarsino) sulfide. Instead the reaction gave the pentacarbonylchromium complex **5e** of this ligand (eq 3).



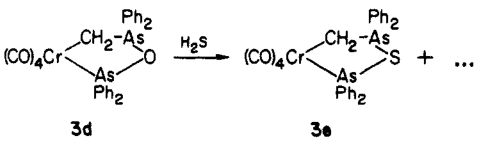
$$1 + \underset{\mathbf{2e}}{(Ph_2As)_2S} \longrightarrow \underset{\mathbf{5e}}{(CO)_5CrAs(Ph)_2SAsPh_2} + \ldots \qquad (3)$$

Again no attempt was made to isolate this compound, and its identity was deduced by comparison of the IR spectrum with that of authentic material which was prepared from pentacarbonyl(η^2-cyclooctene)chromium and **2e** (eq 4).



(4)

However, ylide complex **3d** is easily converted into **3e** when treated with gaseous H_2S in dry dichlormethane (eq 5). The transformation was followed by a color change of the solution from light yellow to red-brown. Workup by chromatography afforded analytically pure **3e** in poor yield.



(5)

The constitutions and configurations of the novel arsonium ylide complexes were deduced from elemental analysis and spectroscopic data. Their IR spectra (CH_2Cl_2) (Table I) show three or four intense metal carbonyl stretching modes which agree with a C_s pseudosymmetry of a $Cr(CO)_4$ moiety.

The highest frequency A′ mode may serve as a probe for the transfer of electron density from the ylidic ligand to the carbonyl group.[21] The donor capacity of the ylides in **3** increases in the series $H_2C{=}As(Ph_2)SAsPh_2 \approx H_2C{=}As(Ph_2)OAsPh_2 \ll H_2C{=}As(Me_2)N(Me)AsMe_2 \approx H_2C{=}As(Ph_2)CH_2AsPh_2 \ll H_2C{=}As(Ph_2)C({=}PPh_3)PPh_2$. Evidence is given that the σ-donor/π-acceptor ratio of the ylide is dependent on the nature of their bridging group between the two arsenic atoms. The incorporation of a second ylide function instead of the CH_2 moiety in **3a** increases the donor capacity of the chelating ligand which is indicated in a long wave shift of the A′ mode by 10 cm^{-1}. On the other hand, the replacement of the CH_2 group by oxygen or sulfur causes a decrease in the donor strength of the ylides. The IR spectra of **3b** and **6b** [ν(CO) 1977 s, 1858 vs, 1810 s cm^{-1}] are comparable, which could be explained by analogous molecular structures of these compounds.

Table I. Carbonyl Stretching Modes (cm^{-1}) of Complexes 3a–e, 4b–e, 5d,e, 8a–d, and 9a,d,e (CH_2Cl_2 Solution)

3a	1990 s, 1874 vs, 1827 s
3b	1980 s, 1868 vs, 1811 s
3c	1991 s, 1860 vs, 1823 s
3d	2001 s, 1908 sh, 1890 vs, 1849 s
3e	2002 s, 1893 vs, 1845 s
4b	1998 s, 1902 s, 1880 vs, 1808 s
4c	2018 s, 1891 vs, 1875 sh, 1850 m
4d	2036 s, 1910 vs
4e	2020 s, 1912 vs, 1890 s
5d	2070 m, 2000 w, 1945 vs, 1890 w
5e	2070 m, 1948 vs
8a	1989 s, 1886 s, 1862 s, 1829 s
8b	1986 s, 1884 s, 1850 s, 1820 s
8c	1990 s, 1885 s, 1865 s, 1829 s
8d	1990 s, 1888 s, 1853 s, 1827 s
9a	2007 m, 1915 sh, 1896 s, 1878 s
9d	2006 m, 1914 sh, 1896 s, 1872 s
9e	2004 m, 1913 sh, 1896 s, 1874 s

The comparison of the IR spectra of **3** and **4** reveals the lesser donor capacity of the bis(arsine) ligands. The similarity of the spectra of **5d** and **5e** indicate the same coordination mode of **2d** and **2e**. Presumably, the ligands are linked to the $(CO)_5Cr$ moiety via one Ph_2As group. In the ^1H NMR experiment compounds **3b,d,e** are characterized by two different signal groups whereas **3c** exhibits four singlets. The protons of the $CrCH_2$ unit absorb at the highest field (0.83–2.57 ppm). Singlets at 1.51 and 1.57 ppm, each accounting for six protons, are due to the two different Me_2As groups in **3c**. In the mass spectra the molecular ions of all new compounds are observed as parent peaks.

(B) Six-Membered Ylide–Chelate Complexes. The synthesis of the desired six-membered metallaheterocycles **8** was conducted by stirring equimolar amounts of **1** and 1,2-ethylenebis(phosphine) or -bis(arsine) in toluene at 60 °C (eq 6). The well-known five-membered chelate complexes **9** are also formed and can be identified on the basis of their infrared spectra in the ν(CO) region. In only two cases (**9d** and **9e**) were these materials isolated.

Compounds **8** are separated from the reaction mixture by fractional crystallization (CH_2Cl_2/hexanes). The complexes are yellow, air stable, and diamagnetic solids, very soluble in all the common organic solvents except saturated hydrocarbons. Complexes **8** are more soluble than the corresponding five-membered analogues $(CO)_4\overline{CrCH_2ER^1{}_2CH_2E}R^2{}_2$.

The thermal stability of the novel complexes decreases in the series **8a** ≈ **8b** > **8c** ≫ **8d**. It is obvious that the compounds **8** are less stable than the chelates $(CO)_4\overline{CrCH_2ER^1{}_2CH_2E}R^2{}_2$.

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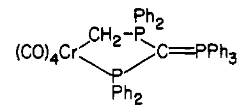
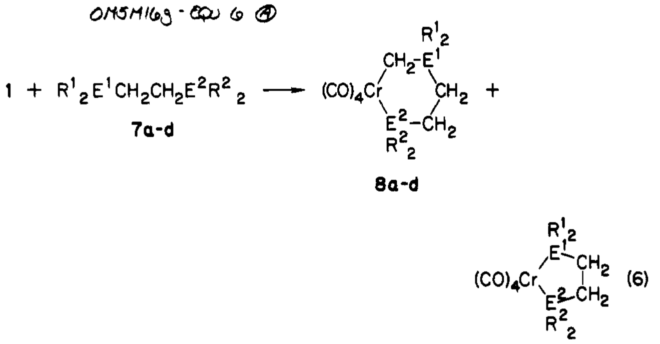
[20] Dobson, G. R.; Brown, R. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2875.

[21] Lindner, E.; Schilling, E.; *Chem. Ber.* **1977**, *110*, 3266.



6b

OM5M16g-EQU 6 Ⓐ

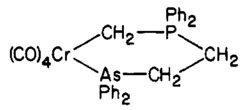


7a-d **8a-d** **9a-d**

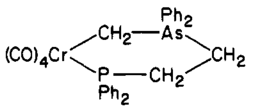
a, $R^1_2E = R^2_2E = Ph_2P$; b, $R^1_2E = R^2_2E = Me_2P$; c, $R^1_2E = Ph_2P$, $R^2_2E = Ph_2As$; d, $R^1_2E = R^2_2E = Ph_2As$

The composition and structure of the chelates **8** were confirmed by elemental analysis and infrared, proton, and phosphorus NMR spectroscopy. Their IR spectra (CH_2Cl_2 solution) display four intense metal carbonyl stretching modes which is in accord with a C_s pseudosymmetry of a $Cr(CO)_4$ moiety (Table I). From the analysis of the ν(CO) frequencies evidence is given that the σ-donor/π-acceptor ratios of the ylides in **8** are comparable to those of the ylides in $(CO)_4CrCH_2ER^1_2CH_2ER^2_2$.[3,4] The comparison of the IR spectra of **8** and **9** reveal the lesser donor capacity of the bis(phosphine) or bis(arsine) ligands.

In the ^{1}H NMR experiment, compounds **8a–d** are characterized by three different signal groups which allow a straightforward assignment on the basis of chemical shifts, multiplicities, and intensities. The protons of the $CrCH_2$ unit absorb at the highest field (−0.20 to +1.12 ppm), and due to coupling to two chemically and magnetically different phosphorus nuclei their signals appear as doublets of doublets (**8a,b**). A coupling constant of 13.3 Hz for the doublet of the $CrCH_2$ protons of **5c** proves the presence of a phosphonium center. With the unsymmetrically substituted ligand **7c** the formation of two isomers **8c** and **8c′** should be possible.



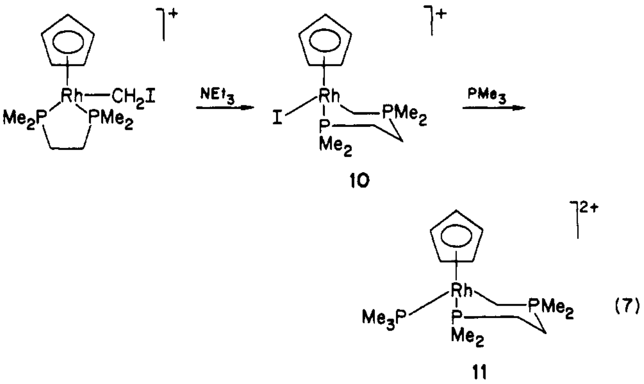
8c



8c′

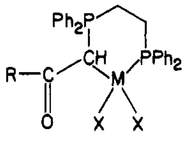
According to the ^{1}H NMR spectrum, however, structure **8c′** is not present. Obviously, the more nucleophilic end of **7c** is transformed into the onium center in **8c**. There is a precedent for this result in the synthesis of $(CO)_4CrCH_2PPh_2CH_2AsPh_2$ from $Ph_2PCH_2AsPh_2$ and **1**. A rationale for the exclusive formation of the phosphonium ylide complex instead of the isomeric arsonium ylide complex is given in the corresponding paper[4] and may also be valid for the generation of **8c**.[4] By consideration of the coupling constants $^2J_{PH}$ both doublets of the *P*-methyl groups of **8b** can be assigned unambigiously ($P^{III}CH_3$, 1.40 ppm, $^2J_{PH} = 6.4$ Hz; P^VCH_3, 1.54 ppm, $^2J_{PH} = 12.5$ Hz).

In the ^{31}P NMR experiment complexes **8a** und **8b** exhibit two doublets (δ 31.68 and 53.00 and δ 22.81 and 31.41, respectively) of equal intensity. By analogy with $(CO)_4CrCH_2PPh_2CH_2PPh_2$ we assign the high-field doublet in **8a** to the phosphonium center, whereas the low-field doublet is due to the metal-coordinated phosphorus atom. On the other hand decoupling experiments on **8b** show that the signal at 31.41 ppm is due to the phosphonium group. The coupling between the two phosphorus atoms in **8a,b** ($J_{PP} = 5$ and 18 Hz, respectively) is considerably smaller than those in the five-membered chelates $(CO)_4CrCH_2PR_2CH_2PR_2$ (R = Ph or Me) ($J_{PP} = 84$ and 81 Hz, respectively). This is to a lesser extent paralleled by the coupling constants in the complexes $Cl_2PdCH[C(O)Ph]P(Ph)_2(CH_2)_2PPh_2$ ($J_{PP} = 24$ Hz) and $Cl_2PdCH[C(O)Ph]P(Ph)_2CH_2PPh_2$ ($J_{PP} = 48$ Hz).[22] Structure **8c** is supported by a ^{31}P NMR peak at 32.29 ppm, which is practically identical with the chemical shift of the phosphonium center in **8a**. Similar results were encountered for $(CO)_4CrCH_2P(Ph)_2CH_2PPh_2$ (P(V), 43.78 ppm) and $(CO)_4CrCH_2P(Ph)_2CH_2AsPh_2$ (P(V), 43.43 ppm).[3,4] Six-membered ylide–chelate complexes with the structural feature $MCH_2ER_2CH_2CH_2ER_2$ are rare and until now were only represented by two rhodium derivatives (**10** and **11**).[23] A novel rearrangement (eq 7) afforded compound **10** but seemed to be limited to dimethylphosphino groups. Arsenic-containing heterocycles of the discussed type are completely unknown.



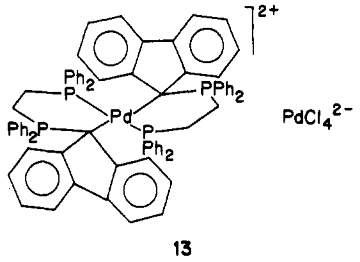
10 **11**

The situation changes when the ylidic carbon atom is substituted by electron-withdrawing groups such as C(O)R (R = Me, Ph, OMe)[22] or where this carbon atom is incorporated into a fluorene system.[24] In these cases the free ylides as well as six-membered Pd(II) and Pt(II) chelates such as **12** and **13** are described in the literature.[22,24]



12

M = Pd, Pt; X = Cl, Br, NCS



13

Conclusion

The transformations described in this paper show that the formation of five-membered ylide–chelate complexes is not limited to phosphorus but also occurs in the chem-

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[22] Oosawa, Y.; Urabe, H.; Saito, T.; Sasaki, Y. *J. Organomet. Chem.* **1976**, *122*, 113.

[23] Werner, H.; Hofmann, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C65.

[24] Holy, N.; Deschler, U.; Schmidbaur, H. *Chem. Ber.* **1982**, *115*, 1379.

istry of arsenic. Functionalities such as phosphonium methanides and amino groups as well as oxygen are tolerated in the ring closure reaction between the sulfonium ylide complex 1 and the corresponding bis(arsine).

Six-membered ylide–chelate complexes are also accessible by this synthetic route when 1,2-ethylenebis(phosphines) and -bis(arsines) are employed.

These results deserve additional attention because the ligands generated here in a template reaction are still unknown as free molecules.

Acknowledgment. This work was generously supported by Fonds der Chemischen Industrie, Frankfurt/Main, West Germany. D.W. is grateful to this institution for a graduate grant. We thank Prof. F. Kober, Universität Darmstadt, for a sample of $(Me_2As)_2NMe$, Prof. N. Kuhn, Universität Duisburg, for a sample of Ph_2AsCl, and Dr. K. Steinbach, Universität Marburg, for mass spectroscopic investigations.

Registry No. 1, 58751-37-4; **2b**, 95531-55-8; **2c**, 50964-61-9; **2d**, 2215-16-9; **2e**, 3134-95-0; **3a**, 83746-96-7; **3b**, 95531-57-0; **3c**, 95531-58-1; **3d**, 95531-59-2; **3e**, 95531-60-5; **4b**, 95531-61-6; **4c**, 95531-62-7; **4d**, 95531-63-8; **4e**, 95531-64-9; **5d**, 95552-52-6; **5e**, 95552-53-7; **7a**, 1663-45-2; **7b**, 23936-60-9; **7c**, 23582-06-1; **7d**, 4431-24-7; **8a**, 95552-54-8; **8b**, 95531-65-0; **8c**, 95531-66-1; **8d**, 95531-67-2; **9a**, 29890-04-8; **9b**, 40544-95-4; **9c**, 40545-10-6; H_2S, 7783-06-4; $Cr(CO)_6$, 13007-92-6; $(CO)_5Cr(C_8H_{14})$, 95531-68-3; chlorodiphenylarsine, 712-48-1; triphenylphosphonium methylide, 19493-09-5; tetracarbonyl(norbornadiene)chromium, 12146-36-0; (*Z*)-cyclooctene, 931-88-4.

A ^{199}Hg FT-NMR and X-ray Structural Study of the Interaction of MeHg^{II} with Pyridines. The Effect of Solvent and Steric Interactions

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A ^{199}Hg FT-NMR study on the extent of complexation of methylmercury with a series of pyridines is described. The formation constants decrease as the steric hindrance around the nitrogen increases in both methylene chloride and nitromethane solvents. However, in methanol solvent one sees a reversal of trends in that the K_f increases on going from pyridine to 2-methylpyridine and levels off with the more hindered 2,6-dimethylpyridine. The increase in complexation is attributed to a ground-state solvation effect on the pyridines. The decrease in hydrogen bonding of the more hindered nitrogenous bases increases their Lewis basicity. An X-ray structural study on the complex of 2-methylpyridine with methylmercury(II) trifluoroacetate shows that the C–Hg–N is nearly linear with trifluoroacetate anion being weakly bound to two mercury atoms forming a losely associated dimeric complex with Hg–O bridging distances of 2.668 (9) and 2.805 (8) Å.

Introduction

The sulfhydryl group has been established to be among the most important binding sites for MeHg^{II} in biological systems.[1] Recently, it has been demonstrated that the imidazole functionality also has a high affinity for methylmercury.[2] This is of particular interest since the imidazole moiety is an integral part of many proteins, and this provides yet another pathway to methylmercury poisoning. Davidson[3] initially showed that DNA was denatured by methylmercury. Subsequently, it was found that MeHg^{II} causes chromosomal damage leading to its mutagenicity.[4] Consequently the interaction of methylmercury and various nitrogenous bases has assumed increased importance.[5,6] Attempts have been made to quantitatively measure the extent of binding of various metal ions with nucleosides and nucleotides.[7] Notable among these are

Table I. Rate Constant Data for Methylation of Pyridines with CH_3I

pyridine	10^5k (25 °C) nitrobenzene[a]	10^4k (60 °C) nitromethane[b]
pyridine	34.3	62.5
2-methylpyridine	16.2	31.3
2,6-dimethylpyridine	1.45	3.36
2-ethylpyridine	7.64	17.1
2-methoxypyridine		NR
2-*tert*-butylpyridine	0.008[c]	

[a] Reference 11. [b] Reference 12. [c] Estimated.

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