208 *Organometallics* **1984**, *3*, 208-211

tillation to remove SO_2 stabilizer. *Caution: HCN is extremely toxic and should be used only in a well-ventilated hood. Heavy rubber gloves should be used, and any contact with skin or clothing should be avoided.* DCN was prepared by slow addition of $NaCN/D_2O$ to a stirred solution of D_3PO_4/D_2O. The liberated DCN was dried by vaporizing it through a tube containing P_2O_5.

Instrumentation. All proton NMR spectra were recorded by using a Varian HA-100 spectrometer. Mass spectra were obtained under electron-impact conditions by using a CEC 21-104 spectrometer. IR spectra were recorded by using a Perkin-Elmer 221 spectrometer. Mono- and dinitrile products were isolated by preparatory GC at 185 °C using a 20 ft × $^1/_4$ in. stainless steel column packed with ECNSS-coated Carbowax 20 M.

Typical Hydrocyanation Procedure. Addition of DCN to 3PN Using $ZnCl_2$ and $Ni[P(O\text{-}p\text{-}tolyl)_3]_4$. A 50-mL, three-neck, round-bottom flask was equipped with Teflon-coated stirring bar, heating mantle, thermometer, N_2-inlet tube, and N_2-outlet tube. The flask was charged with 26 mL (266 mmol) of 3PN, 8.5 mL (26.6 mmol) of $P(O\text{-}p\text{-}tolyl)_3$, 0.27 g (2.0 mmol) of $ZnCl_2$, and 1.8 g (1.2 mmol) of $Ni[P(O\text{-}p\text{-}tolyl)_3]_4$. The temperature of the stirred solution was adjusted to 60 °C. A glass 10-mL bubbler was immersed in a wet ice bath and was charged with 5 mL of ice-cold DCN. A flow of N_2 through the DCN was adjusted to vaporize 1.0 mL/h (0.6 mmol/h) of DCN into the inlet tube of the reactor. Following vaporization of the DCN, the reaction mixture was filtered and distilled to give a mixture of dinitrile products. Separate samples of ADN-*d* and MGN-*d* were obtained by preparatory GC for ^1H NMR analysis.

^1H NMR Analysis of Dinitrile Products for Deuterium Incorporation. ^1H NMR spectra of 10–50-μL fractions of dinitrile products, dissolved in $CDCl_3$ with Me_4Si internal standard, were obtained and peak integrals were recorded. Reference ^1H NMR spectra of undeuterated dinitriles were used for calculation of amounts of deuteration, by differences in integrals of reference and deuterated compounds. Table IV gives an analysis of dinitrile products obtained by $Ni[P(O\text{-}p\text{-}tolyl)_3]_4$-catalyzed addition of DCN to 3PN at 68 °C, using $AlCl_3$.

Registry No. 4PN, 592-51-8; 3PN, 4635-87-4; 2PN, 13284-42-9; 2Me3BN, 16529-56-9; $ZnCl_2$, 7646-85-7; $AlCl_3$, 7446-70-0; BPh_3, 960-71-4; $HNi[P(OEt)_3]_3CNZnCl_2$, 87655-30-9; $HNi[P(OEt)_3]_4^+\cdot CNZnCl_2^-$, 25358-26-3; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)_3]_3CNZnCl_2$, 87655-31-0; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)_3]_4^+\cdot CNZnCl_2^-$, 87727-23-9; $HNi[P(OEt)_3]_3CN$, 59284-99-0; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)_3]_3CN$, 25358-27-4; $HNi[P(OEt)_3]_3CNAlCl_3$, 87655-32-1; $HNi[P(OEt)_3]_4^+\cdot CNAlCl_3^-$, 87758-25-6; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)_3]_3CNAlCl_3$, 87655-33-2; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)_3]_4^+\cdot CNAlCl_3^-$, 87727-24-0; $HNi[P(OEt)_3]_3CNBPh_3$, 87655-34-3; $HNi[P(OEt)_3]_4^+\cdot CNBPh_3^-$, 87727-25-1; $HNi[P(O\text{-}p\text{-}MeOC_6H_4)\text{-}CNBPh_3$, 87655-35-4; $Ni[P(OEt_3)]_4$, 14839-39-5; $Ni[P(O\text{-}p\text{-}tolyl)_3]_4$, 36700-08-0; $Ni[P(O\text{-}p\text{-}MeOC_6H_4)_3]_4$, 14285-90-6; hydrogen, 1333-74-0.

Transfer of Hydrogen from Carbon–Hydrogen Bonds. Synthesis, Structure, and Reactions of Tris[(triphenylstannyl)methyl]methane[1]

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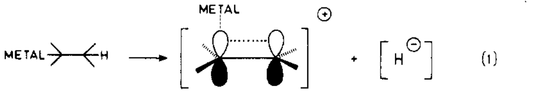
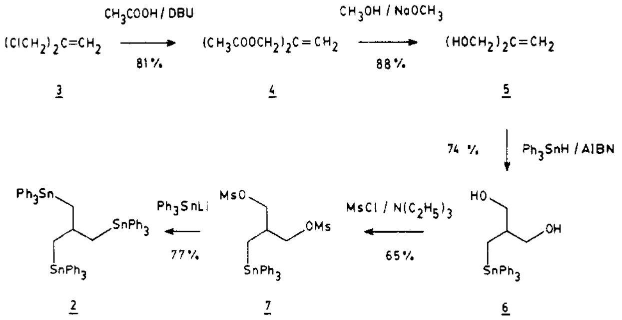
Compounds in which a carbon–hydrogen bond is adjacent to several carbon–metal bonds promise to be particularly good donors of hydrogen. The synthesis, structure, and redox reactions of one member of this group of compounds, tris[(triphenylstannyl)methyl]methane (2), are reported. Triphenylcarbenium is reduced to triphenylmethane less rapidly by stannane 2 than by bis[(triphenylstannyl)methyl]methane (11). The unexpectedly low reactivity of stannane 2 is due to the adoption of a C_3 conformation in which the central carbon–hydrogen bond is sterically shielded and gauche to the adjacent carbon–tin bonds.

The transfer of hydrogen from a carbon–hydrogen bond is an important and deceptively simple process.[2] To see how favorable this reaction can be when circumstances are ideal, we have begun to study covalent compounds designed to be particularly good donors of hydride or hydrogen.[3] Compounds in which a carbon–hydrogen bond is adjacent to a carbon–metal bond are promising candidates, since loss of hydride or hydrogen may lead to a carbocation or radical stabilized by hyperconjugation (eq 1).[4,5] If an intermediate is actually formed,[6] it can be further stabilized by increasing the number of adjacent carbon–metal bonds. We have therefore begun to study the ability of tris(metallomethyl)methanes (1) to serve as formal donors of hydride. This ability should increase as



(1)

Scheme I



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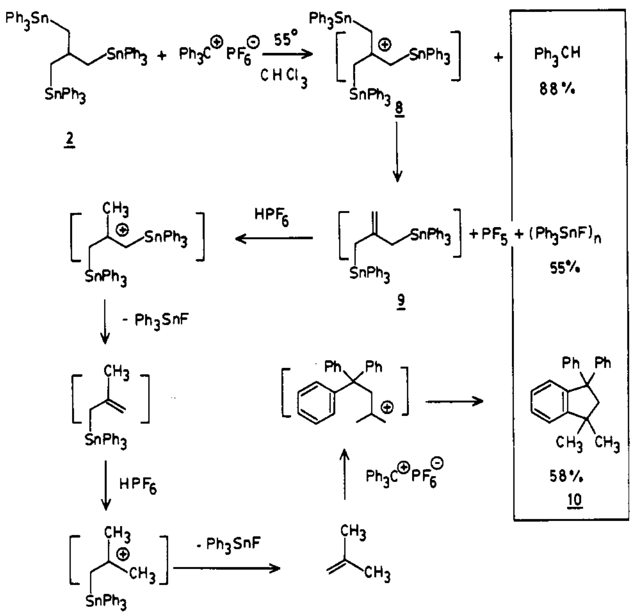
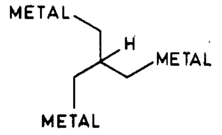
Scheme II



the metal becomes more electropositive and as the absolute value of $\sigma+$ for the metallomethyl group increases. Because $\sigma+$ for the group (triphenylstannyl)methyl (Ph_3SnCH_2) is relatively large (−0.73)[7] and because organotin compounds are reasonably easy to prepare and characterize, we made tris[(triphenylstannyl)methyl]methane (**2**)[8] our inital target.



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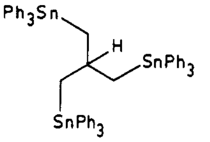


2

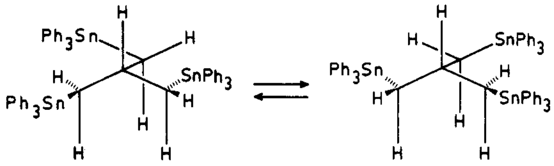
The synthesis of stannane **2** is summarized in Scheme I. Conversion of 3-chloro-2-(chloromethyl)-1-propene (**3**) into diacetate **4**,[9] followed by methanolysis, conveniently provided the known diol **5**.[10] Hydrostannation with triphenyltin hydride led to stannane **6**, which was converted into dimesylate **7**. Reaction of this compound with (triphenylstannyl)lithium then produced tris[(triphenylstannyl)methyl]methane (**2**).

In chloroform at 55 °C, stannane **2** slowly reduced triphenylcarbenium hexafluorophosphate to triphenylmethane in 88% yield. Hypothetical Scheme II describes this reaction in more detail. Cation **8** could not be detected by NMR, so it is absent or short-lived. If cation **8** is formed, it may be converted into 2-methylene-1,3-propanediylbis[triphenylstannane] (**9**)[6c] by the rapid loss of triphenyltin fluoride. The high sensitivity of stannane **9** to electrophilic attack presumably prevented its isolation or detection and facilitated its conversion into isobutylene by sequential protonations and losses of triphenyltin fluoride.[6c] Evidence for these steps comes from the following observations. Triphenyltin fluoride in fact precipitated from the reaction mixture and could be isolated in 55% yield (based on the formation of 3 mol/mol of stannane **2**). Isobutylene, which could be detected directly by NMR, ultimately reacted with excess triphenylcarbenium hexafluorophosphate to give 1,1-dimethyl-3,3-diphenylindan (**10**)[11] in 58% yield.

Although stannane **2** reduces triphenylcarbenium, the following experiment shows that it is not an unusually good donor of hydride. In this experiment, we compared the rates of reduction of triphenylcarbenium tetrafluoroborate by bis- and tris[(triphenylstannyl)methyl]methane (compounds **11**[12] and **2**).[13] If loss of hydride from these stan-

$$\underset{\mathbf{11}}{(Ph_3SnCH_2)_2CH_2} \qquad \underset{\mathbf{2}}{(Ph_3SnCH_2)_3CH}$$

nanes produces cationic intermediates and if all of the carbon–tin bonds can participate in hyperconjugation, then the expected order of reactivities is **11** < **2**. In fact, stannane **11** reacts seven times *faster* than stannane **2** in chloroform at 25 °C. We attribute this unexpected observation to the following factors. Molecular models strongly suggest that the large triphenyltin groups[14] will (1) force stannane **2** to adopt the enantiomeric C_3 conformations **12** and **12′** and (2) severely inhibit full rotation about the three carbon–carbon single bonds of stannane **2**. Since the ^{119}Sn NMR spectrum at 25 °C consists of a singlet, an axis of effective C_3 symmetry is in fact present. The methylene hydrogens are also equivalent at 25 °C, so the interconversion of conformers **12** and **12′** probably is fast. Furthermore, X-ray crystallography confirms that stannane **2** prefers a very similar conformation in the solid state, although minor deviations from perfect C_3 symmetry are present.[15] This preference has two consequences. One



12 12′

is that the methine hydrogen is shielded by three triphenyltin groups and made sterically inaccessible. The second is that all three carbon–tin bonds are gauche to the central carbon–hydrogen bond. Since the elegant and extensive work of Traylor has demonstrated that the formal loss of hydride from stannanes is fastest when the carbon–tin and carbon–hydrogen bonds are anti periplanar,[16] stannane **2** is not an ideal source of hydride. As a result, we are now studying tris(metallomethyl)methanes which adopt the more reactive conformation **13**.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 710B spectrometer. Brüker WH-90 or WH-400 spectrometers were used to obtain ^1H and ^{119}Sn nuclear magnetic resonance (NMR) spectra. Chemical shifts for ^1H and ^{119}Sn are reported in parts per million downfield from internal tetramethylsilane and external tetramethyltin (δ), respectively. Mass spectra were

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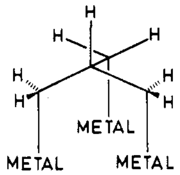

13

recorded at 70 eV on a V.G. Micromass 12–12 quadrupole spectrometer using electron impact (EI) or chemical ionization (CI) or on a Kratos MS-50 instrument using fast atom bombardment (FAB). Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Glassware was dried at 120 °C and cooled under dry Ar immediately before use. Tetrahydrofuran was distilled from the sodium ketyl of benzophenone, and chloroform and dichloromethane were distilled from phosphorus pentoxide. All other reagents were commercial products of the highest purity obtainable.

2-Methylene-1,3-propanediol Diacetate (4).[9] A stirred solution of acetic acid (6.93 g, 115 mmol) in benzene (25 mL) was treated at 25 °C with a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (16.4 g, 108 mmol) in benzene (25 mL). The yellow mixture was then added during 10 min to a solution of 3-chloro-2-(chloromethyl)-1-propene (5.10 g, 40.8 mmol) in benzene (50 mL), and the mixture was warmed at 60 °C for 72 h. A white precipitate was then removed by filtration and washed with benzene, and the combined benzene phases were washed with water and dried. Evaporation of solvent under reduced pressure left a residue of yellow oil. Distillation of this residue under vacuum gave an analytically pure sample of 2-methylene-1,3-propanediol diacetate, a colorless liquid (**4**; 5.66 g, 32.9 mmol, 80.6%): bp 148 °C (70 torr); IR (liquid film) 1740, 1600, 1240 cm^{-1}; ^{1}H NMR (90 mHz, $CDCl_3$) δ 2.09 (s, 6 H), 4.61 (s, 4 H), 5.28 (s, 2 H); mass spectrum (CI), *m/e* 173. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.03; O, 37.16. Found: C, 55.72; H, 7.12.

2-Methylene-1,3-propanediol (5).[10] A stirred solution of 2-methylene-1,3-propanediol diacetate (**4**; 5.53 g, 32.1 mmol) in methanol (20 mL) was treated at 0 °C with a solution of sodium methoxide (10 mmol) in methanol (3 mL). The mixture was kept at 0 °C for 2 h and then at 25 °C for 48 h. Solvent was removed by evaporation under reduced pressure, and distillation of the residue provided 2-methylene-1,3-propanediol as a colorless liquid (**5**; 2.50 g, 28.4 mmol, 88.5%): bp 156 °C (63 torr) (lit.[10] 127–129 °C (32 torr)).

2-[(Triphenylstannyl)methyl]-1,3-propanediol (6). A mixture of 2-methylene-1,3-propanediol (**5**; 1.12 g, 12.7 mmol), triphenyltin hydride (4.53 g, 12.9 mmol), and AIBN (55.7 mg, 0.339 mmol) was warmed under Ar for 5 h at 64 °C. Direct crystallization of the solid product from a mixture of hexanes (50 mL) and benzene (26 mL) provided colorless, analytically pure crystals of 2-[(triphenylstannyl)methyl]-1,3-propanediol (**6**; 4.12 g, 9.38 mmol, 73.9%): mp 122.0–122.5 °C; IR (KBr) 3560, 3300, 1420, 1070, 720, 690 cm^{-1}; ^{1}H NMR (90 mHz, $CDCl_3$) δ 1.39 (d, 2 H), 2.2 (m, 1 H), 3.6 (m, 4 H), 7.3–7.6 (m, 15 H); mass spectrum (CI), *m/e* 363, 351, 285, 197, 154, 120. Anal. Calcd for $C_{22}H_{24}O_2Sn$: C, 60.18; H, 5.51. Found: C, 60.43; H, 5.73.

2-[(Triphenylstannyl)methyl]-1,3-propanediol Dimethanesulfonate (7).[17] A stirred solution of 2-[(triphenylstannyl)methyl]-1,3-propanediol (**6**; 999 mg, 2.27 mmol) and triethylamine (508 mg, 5.02 mmol) in dichloromethane (200 mL) was treated dropwise at 0 °C with methanesulfonyl chloride (521 mg, 4.55 mmol). The reaction mixture was kept at 0 °C for 4 h, diluted with dichloromethane (50 mL), and then washed at 0 °C with water, 1.0 N aqueous HCl, and saturated aqueous $NaHCO_3$. The organic phase was dried, and solvent was removed by evaporation under reduced pressure. Crystallization of the residue from a mixture of hexanes and benzene produced colorless, analytically pure needles of 2-[(triphenylstannyl)methyl]-1,3-propanediol dimethanesulfonate (**7**; 880 mg, 1.48 mmol, 65.2%): mp 121.0–121.5 °C; IR (KBr) 1340, 1175 cm^{-1}; ^{1}H NMR (90 mHz, $CDCl_3$) δ 1.51 (d, 2 H), 2.5 (m, 1 H), 2.78 (s, 6 H), 4.16 (d of d, 4 H), 7.3–7.6 (m, 15 H); mass spectrum (EI), *m/e* 369, 351, 292, 197, 154, 120. Anal. Calcd for $C_{24}H_{28}O_6S_2Sn$: C, 48.42; H, 4.74. Found: C, 48.51; H, 4.85.

2-[(Triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2). Under dry Ar at 0 °C, a stirred solution of (triphenylstannyl)lithium[18] (22 ml, 0.24 M in THF, 5.3 mmol) was treated dropwise with a solution of 2-[(triphenylstannyl)methyl]-1,3-propanediol dimethanesulfonate (**7**; 1.26 g, 2.12 mmol) in THF (6 mL). The mixture was kept at 25 °C for 18 h and warmed at reflux for 3 h, and then water (0.5 mL) was added. Volatiles were removed by evaporation under reduced pressure, and the residue was partitioned between water (200 mL) and dichloromethane (400 mL). The organic phase was dried, and solvent was removed by evaporation under reduced pressure. Careful gradient flash chromatography[19] of the residue (silica, hexanes (95%)/chloroform (5%)–hexanes (75%)/chloroform (25%)) provided pure 2-[(triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (**2**; 1.80 g, 1.63 mmol, 76.9%). Crystallization from hexanes (50%)/ethyl acetate (50%) afforded an analytically pure sample: mp 206.5–208.0 °C; IR (KBr) 1420, 1070, 720, 690 cm^{-1}; ^{1}H NMR (400 mHz, $CDCl_3$) δ 1.76 (d, ^3J(H,H) = 7.1 Hz, average ^2J(^{117,119}Sn,H) = 55 Hz, 6 H), 2.63 (m, ^3J(H,H) = 7.1 Hz, average ^3J (^{117,119}Sn,H) = 44 Hz, 1 H), 7.2–7.4 (m, 45 H); ^{119}Sn NMR (400 mHz, 5% CD_2Cl_2 in CH_2Cl_2) δ −107.9 (s, gated proton decoupling; broad q, selective decoupling of aromatic protons); mass spectrum (FAB), *m/e* 1108, 1031. Anal. Calcd for $C_{58}H_{52}Sn_3$: C, 63.04; H, 4.74. Found: C, 63.23; H, 4.79.

Reduction of Triphenylcarbenium Hexafluorophosphate by 2-[(Triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2). A mixture of 2-[(triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (**2**; 18.9 mg, 17.1 μmol) and triphenylcarbenium hexafluorophosphate (25.5 mg, 65.7 μmol) in chloroform (2 mL) was sealed in a tube under vacuum and warmed at 55 °C for 65 h. The tube was opened, and centrifugation separated a white precipitate of triphenyltin fluoride (10.4 mg, 28.2 μmol, 55.0% based on the formation of 3 mol/mol of stannane **2**). Volatiles were removed from the supernatant by evaporation under reduced pressure, and preparative thin-layer chromatography (silica, hexanes (67%)/benzene (33%)) separated the residue into two major components. One was triphenylmethane (3.7 mg, 15 μmol, 88%, R_f 0.66); the other was 1,1-dimethyl-3,3-diphenylindan (**10**; 2.9 mg, 10 μmol, 58%, R_f 0.72), which by NMR, IR, and mass spectrometry was identical with an authentic sample.[11]

1,3-Propanediylbis[triphenylstannane] (11).[12] Under dry N_2 at 0 °C, a stirred solution of (triphenylstannyl)lithium[18] (78 mL, 0.23 M in THF, 18 mmol) was treated dropwise with a solution of 1,3-dibromopropane (1.6 g, 7.9 mmol) in THF (20 mL). The mixture was kept at 25 °C for 18 h and warmed at reflux for 3 h, and then water (1.0 mL) was added. Volatiles were removed by evaporation under reduced pressure, and the residue was partitioned between water (1000 mL) and chloroform (300 mL). The organic phase was dried, and solvent was removed by evaporation under reduced pressure. Crystallization of the residue once from methanol and then once from hexanes yielded a purified sample of 1,3-propanediylbis[triphenylstannane] (**11**; 2.2 g, 3.0 mmol, 38%). A third crystallization from methanol provided an analytically pure sample: mp 100–101 °C; IR (KBr) 1420, 1070, 720, 690 cm^{-1}; ^{1}H NMR (90 mHz, $CDCl_3$) δ 1.60 (m, 4 H), 2.1 (m, 2 H), 7.3–7.6 (m, 30 H); mass spectrum (CI), *m/e* 667, 351, 274, 197, 120. Anal. Calcd for $C_{39}H_{36}Sn_2$: C, 63.12; H, 4.89; Sn, 31.99. Found: C, 62.99; H, 5.06; Sn, 31.69.

Reduction of Triphenylcarbenium Hexafluorophosphate by 1,3-Propanediylbis[triphenylstannane] (11). A mixture of 1,3-propanediylbis[triphenylstannane] (**11**; 288 mg, 0.388 mmol) and triphenylcarbenium hexafluorophosphate (597 mg, 1.54 mmol) in chloroform (40 mL) was stirred under Ar at 25 °C for 17 h. Centrifugation then separated a white solid, which was washed with 50% aqueous acetone. The insoluble material was tri-

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phenyltin fluoride (126 mg, 0.341 mmol, 43.9% based on the formation of 2 mol/mol of stannane 11). Volatiles were removed from the supernatant by evaporation under reduced pressure, giving a residue which contained allyltriphenylmethane[20] and triphenylmethane (90% yield by NMR). These two compounds could not be separated by thin-layer chromatography under a variety of conditions, but careful molecular distillation at 65 °C (0.15 torr) yielded pure triphenylmethane (33.6 mg, 0.138 mmol, 35.6%). Further distillation at 85 °C (0.13 torr) yielded allyltriphenylmethane (32.8 mg, 0.120 mmol, 30.9%), which by NMR, IR, and mass spectrometry was identical with an authentic sample.[20,21]

Relative Rates of Reduction of Triphenylcarbenium Tetrafluoroborate by 2-[(Triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2) and 1,3-Propanediylbis[triphenylstannane] (11). A mixture of 2-[(triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2; 5.5 mg, 5.0 μmol) and diphenylmethane (3.4 mg, 20 μmol), added as an internal standard, was treated under Ar with a solution of triphenylcarbenium tetrafluoroborate in deuteriochloroform (0.80 mL, 0.074 M, 59 μmol). The resulting solution was kept at 25 °C, and the rate of formation of triphenylmethane was measured by NMR.

An analogous experiment yielded the rate of reduction of triphenylcarbenium tetrafluoroborate by 1,3-propanediylbis[triphenylstannane] (11).

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Registry No. 2, 87549-81-3; 3, 1871-57-4; 4, 3775-29-9; 5, 3513-81-3; 6, 87597-80-6; 7, 87597-81-7; 11, 86623-72-5; Ph_3SnLi, 4167-90-2; Ph_3SnH, 892-20-6; $Ph_3C^+PF_6^-$, 437-17-2; 1,3-dibromopropane, 109-64-8.

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[20] Formation of allyltriphenylmethane can be attributed to the reaction of excess triphenylcarbenium hexafluorophosphate with allyltriphenylstannane. For a very similar observation, see: Kashin, A. N.; Bumagin, N. A.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *171*, 321-331.

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He I and He II Photoelectron Spectroscopic Studies of the Bonding in Cobalt, Rhodium, and Iridium Cyclopentadienyl Diene Complexes

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He I and He II photoelectron spectra have been obtained for a series of cobalt, rhodium, and iridium complexes where the metal is bonded both to a cyclopentadienyl group and to a diene system, $M(\eta\text{-}C_5R_5)L_2$: M = Co, R = H, L_2 = (η^4-cycloocta-1,5-diene), IV, L_2 = (η^4-cyclohexa-1,3-diene), VI; M = Co, R_5 = Me_4Et, L_2 = (η^4-cycloocta-1,5-diene), IVa; M = Rh, R = H, L_2 = (η^4-buta-1,3-diene), I, L_2 = (η^4-cycloocta-1,5-diene), V, L_2 = (η^4-cyclohexa-1,3-diene), VII, L_2 = (η^4-cyclooctatetraene), VIII; M = Rh, R = Me, L_2 = (η^4-cycloocta-1,5-diene), Va, L = C_2H_4, IX; M = Ir, R = H, L_2 = (η^4-buta-1,3-diene), II, L_2 = (η^4-2-methylbuta-1,3-diene), III. Ionization energy trends and intensity patterns are used to assign the spectra on the basis of a qualitative MO scheme. The nature of the HOMO is found to vary markedly from the Co complexes to the Rh and Ir complexes. In the cobalt cases the HOMO is largely d in character, whereas for Rh and Ir substantial localization on the ligands is indicated. These differences in electronic structure can be correlated with differences in chemical behavior. The preference of the metal–cyclopentadienyl unit for bonding to nonconjugated dienes is discussed.

Introduction

There have been several investigations of the photoelectron spectra of dienes and diolefins bonded to transition metals.[1-9] Most of the studies of dienes were on complexes of the type $M(CO)_3L_2$, where M = Fe or Ru,[1-4,6-8] whereas that on the diolefins was of compounds of the type M(β-diketonate)L_2, where M = Rh or Ir.[9] There also exists a large class of volatile diene complexes of the type $M(\eta\text{-}C_5R_5)L_2$, where M = Co, Rh, and Ir, in which the metal center would be expected to be more

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