Organosilicon-Based Multifunctional β-Diketones and their Rhodium and Iridium Complexes

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Six new organosilicon-based bis-, tris-, and tetrakis(β-diketones) and their Rh^{I}(COD) and Ir^{I}(COD) (COD = 1,5-cyclooctadiene) complexes have been prepared and characterized. The β-diketones, $(CH_3)_{4-n}Si(4\text{-}C_6H_4CH(COR)_2)_n$ ($n = 2, 3, 4$; R = Me, Et), were prepared from the corresponding aldehydes $(CH_3)_{4-n}Si(4\text{-}C_6H_4CHO)_n$ by reaction with trimethyl phosphite-α-diketone adducts. Reaction with $[M(COD)(\mu\text{-}Cl)]_2$ (M = Rh and Ir) produces the Rh and Ir complexes, three of which have been characterized by X-ray analysis. The β-diketone moieties are ca. 13.3 Å apart, which leads to intramolecular M$\cdots$M distances in the complexes averaging ca. 15.6 Å. The present organosilicon-based route is expected to be useful for the construction of a variety of polytopic molecules containing either β-diketone or other functional groups and polygonal or polyhedral metal complexes based on them.

Introduction

The design and synthesis of metal-organic compounds is a rapidly growing area of study because there are many promising fragments available for the construction of supramolecular materials.[1−6] These materials are most often prepared by first synthesizing multifunctional organic ligands (sometimes called “linkers” or “building blocks”) and then treating them with metal ions. We are interested in building blocks based on β-diketonate ligands, because they offer the stability of chelation as well as the opportunity for symmetrical placement of substituents.[7]

We now report a family of tetrahedral building blocks that have two, three, and four β-diketone moieties; these react further with metal salts to form polynuclear metal complexes as shown in Figure 1. The building blocks are designed for the synthesis of structurally defined metal-organic frameworks (MOFs), including both molecular and network-solid materials. The present work represents the first steps toward achieving that goal. We used organosilicon chemistry because it provides a simple and efficient synthetic route to multifunctional β-diketones. We also converted the new β-diketones into their polynuclear Rh and Ir complexes, which are stable in the solid state. Three of the Rh complexes have also been characterized by X-ray crystallography, which reveals intramolecular Si$\cdots$Rh and Rh$\cdots$Rh distances averaging 9.6 and 15.6 Å, respectively, and Rh$\cdots$Si$\cdots$Rh angles averaging ca. 109°, as expected for approximately tetrahedral structures. The approach outlined here is expected to be valuable for the preparation of molecules containing both β-diketone and other functional groups at well-defined distances and orientations and for their subsequent conversion to polynuclear metal complexes.

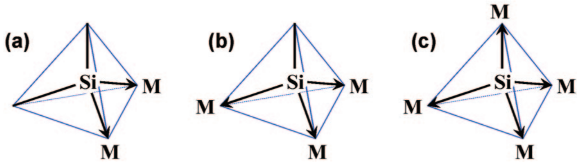

Figure 1. Sketch of the polynuclear metal complexes that can form when tetrahedral organosilicon-based (a) bis-, (b) tris-, and (c) tetrakis(β-diketones) react with metal ions.

Experimental Section

General Considerations. Reagents were used as received: 4-bromobenzaldehyde dimethyl acetal and $SiCl_4$ (Aldrich), dimethyldichlorosilane and methyltrichlorosilane (Gelest Inc.), $CDCl_3$ (Fisher), $[Rh(COD)(\mu\text{-}Cl)]_2$ (Strem), and $[Ir(COD)(\mu\text{-}Cl)]_2$ (COD = 1,5-cyclooctadiene) (Pressure Chemicals). Column chromatography was carried out with Sorbent Technologies silica gel (230−450 mesh). NMR spectra were recorded on Bruker (250, 300, or 400 MHz) or Varian (500 MHz) spectrometers, with $CDCl_3$ as solvent unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. The phospholenes 2,2,2-trimethoxy-4,5-dimethyl-[8] and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene,[9] and bis(4-formylphenyl)dimethylsilane ($(CH_3)_2Si(4\text{-}C_6H_4CHO)_2$),[10] were prepared by literature methods.

Tris(4-formylphenyl)methylsilane ($CH_3Si(4\text{-}C_6H_4CHO)_3$). 4-Bromobenzaldehyde dimethyl acetal (12.02 g, 52.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 32.5 mL, 52 mmol) was added at −78 °C over 40 min. After stirring for an additional 90 min at −78 °C, methyl-

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trichlorosilane (1.40 mL, 13.2 mmol) was slowly added to the above suspension. The reaction mixture was stirred for an additional 2 h at −78 °C and then overnight while it returned to room temperature. The reaction mixture was quenched with 2 M HCl (60 mL) and extracted with ether (3 × 50 mL). The ether solution was washed with brine, dried over $MgSO_4$, and evaporated to give the oily intermediate acetal $CH_3Si(4\text{-}C_6H_4CH(OCH_3)_2)_3$, which was hydrolyzed without purification. The oil was dissolved in 100 mL of THF/2 M HCl (1:1 v/v) and the mixture refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured into saturated $NaHCO_3$(aq) (50 mL) and extracted with ether (3 × 50 mL). The combined extract was washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure, giving an oil. The crude product was purified by column chromatography (hexane/ethyl acetate, 3:1) to give tris(4-formylphenyl)methylsilane as a colorless liquid, 2.67 g (56%). ^{1}H NMR: δ 10.07 (s, 3H, CHO); 7.90, 7.68 (AB, 12H, aromatic CH); 0.97 (s, 3H, $SiCH_3$). ^{13}C NMR: δ 192.6, 142.63, 137.4, 135.9, 129.2, −3.7. ^{29}Si NMR: −11.3. FTIR: 3030, 2831, 1698, 1595, 1209, 838 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_3Si$ (M = 358.46): C, 73.71; H, 5.06. Found: C, 73.45; H, 5.11.

Tetrakis(4-formylphenyl)silane ($Si(4\text{-}C_6H_4CHO)_4$). 4-Bromobenzaldehyde dimethyl acetal (12.02 g, 52.0 mmol) was dissolved in dry THF (150 mL) under nitrogen. n-BuLi solution in hexane (1.6 M, 32.5 mL, 52 mmol) was added slowly at −78 °C over 45 min. After stirring the mixture for 2 h at −78 °C, tetrachlorosilane (1.14 mL, 10 mmol) was slowly added to the above suspension. The remainder of the procedure up to the isolation of the crude product was the same as that for $CH_3Si(4\text{-}C_6H_4CHO)_3$, except that the crude $Si(4\text{-}C_6H_4CHO)_4$ was obtained as an off-white solid. This was recrystallized from hexane/ethyl acetate (3:1) to give ($Si(4\text{-}C_6H_4CHO)_4$) as a white solid, 3.40 g (75%), mp 200−204 °C. ^{1}H NMR: δ 10.09 (s, 4H, C*H*O); 7.94, 7.73 (*AB*, 16H, aromatic C*H*). ^{13}C NMR: δ 192.3, 139.7, 137.9, 137.0, 129.3. ^{29}Si NMR: −16.9. FTIR: 3057, 2830, 1701, 1597, 1208, 837 cm^{-1}. Anal. Calcd for $C_{28}H_{20}O_4Si$ (M = 448.54): C, 74.98; H, 4.49. Found: C, 74.72; H, 4.60.

3,3′-[Dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedione), $(CH_3)_2Si(phacH)_2$ (1). A mixture of bis(4-formylphenyl)dimethylsilane (2.19 g, 8.16 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (4.29 g, 20.4 mmol) was stirred at room temperature under argon. After 24 h, 50 mL of methanol was added, and the mixture was refluxed under nitrogen for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **1** as a white solid, 1.95 g (58%), mp 155−157 °C. ^{1}H NMR: δ 16.70 (s, 2H, O*H*); 7.55, 7.18 (*AB*, 8H, aromatic C*H*); 1.92 (s, 12H, C*H*$_3$); 0.60 (s, 6H, SiC*H*$_3$). ^{13}C NMR: δ 191.1, 137.9, 137.8, 134.8, 130.7, 115.3, 24.5, −2.0. ^{29}Si NMR: δ 10.0. Anal. Calcd for $C_{24}H_{28}O_4Si$ (M = 408.55): C, 70.55; H, 6.91. Found: C, 70.70; H, 7.02.

4,4′-[Dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedione), $(CH_3)_2Si(phprH)_2$ (2). A mixture of bis(4-formylphenyl)dimethylsilane (1.00 g, 3.73 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (2.66 g, 11.2 mmol) was stirred at room temperature under argon. After 18 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **2** as a white solid, 0.71 g (41%), mp 98−99 °C. ^{1}H NMR: δ 16.72 (s, 2H, O*H*); 7.52, 7.15 (*AB*, 8H, aromatic C*H*); 2.11 (m, 8H, C*H*$_2$) 1.01 (t, 12H, C*H*$_3$); 0.56 (s, 6H, SiC*H*$_3$). ^{13}C NMR: δ 194.1, 137.2, 137.0, 134.5, 130.7, 113.8, 29.9, 9.6, −2.2. ^{29}Si NMR: δ 13.1. Anal. Calcd for $C_{28}H_{36}O_4Si$ (M = 464.66): C, 72.37; H, 7.81. Found: C, 72.21; H, 7.64.

3,3′,3″-[Methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedione), $CH_3Si(phacH)_3$ (3). A mixture of tris(4-formylphenyl)methylsilane (1.76 g, 4.91 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (4.60 g, 21.9 mmol) was stirred at room temperature under argon. After 20 h, 60 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid formed. It was collected and air-dried. The filtrate was concentrated under reduced pressure to about 10 mL and filtered, giving a second crop of product. The combined product was recrystallized from methanol to give **3** as a white solid, 1.56 g (56%), mp 212−215 °C. ^{1}H NMR: δ 16.71 (s, 3H, O*H*); 7.55, 7.21 (*AB*, 12H, aromatic C*H*); 1.93 (s, 18H, C*H*$_3$); 0.91 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 191.1, 138.4, 135.8, 135.1, 130.9, 115.3, 24.5, −2.9. ^{29}Si NMR: δ 12.5. Anal. Calcd for $C_{34}H_{36}O_6Si$ (M = 568.72): C, 71.80; H, 6.38. Found: C, 72.00; H, 6.47.

4,4′,4″-[Methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedione), $CH_3Si(phprH)_3$ (4). A mixture of tris(4-formylphenyl)methylsilane (0.390 g, 1.09 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (1.00 g, 4.20 mmol) was stirred at room temperature under argon. After 20 h, 10 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. Then solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give **4** as a white solid, 0.385 g (54%), mp 130−132 °C. ^{1}H NMR: δ 16.76 (s, 3H, O*H*); 7.55, 7.21 (*AB*, 12H, aromatic C*H*); 2.16 (m, 12H, C*H*$_2$) 1.05 (t, 18H, C*H*$_3$), 0.91 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 194.0, 137.7, 135.6, 134.8, 130.8, 113.7, 30.0, 9.6, −3.0. ^{29}Si NMR: δ 12.4. Anal. Calcd for $C_{40}H_{48}O_6Si$ (M = 652.87): C, 73.58; H, 7.41. Found: C, 73.47; H, 7.37.

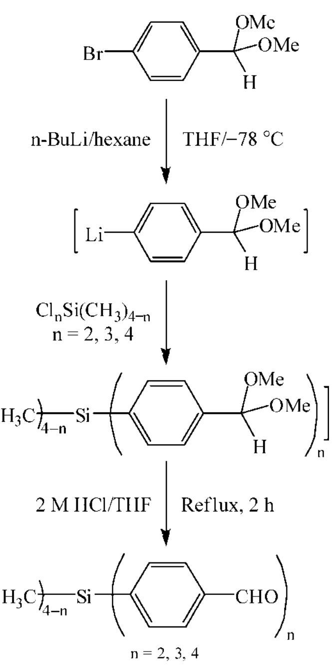
3,3′,3″,3‴-[Silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedione), $Si(phacH)_4$ (5). A mixture of tetrakis(4-formylphenyl)silane (2.00 g, 4.46 mmol) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (5.60 g, 26.8 mmol) was stirred at room temperature under argon. After 20 h, 60 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid appeared. After cooling, the mixture was filtered, giving solid **5** as a pure white solid compound, 1.91 g (59%), mp >220 °C. ^{1}H NMR: δ 16.72 (s, 4H, O*H*); 7.61, 7.26 (*AB*, 16H, aromatic C*H*), 1.94 (s, 24H, C*H*$_3$). ^{13}C NMR: δ 191.0, 138.8, 136.9, 133.1, 131.0, 115.2, 24.5. ^{29}Si NMR: δ 16.6. Anal. Calcd for $C_{44}H_{44}O_8Si$ (M = 728.90): C, 72.50; H, 6.08. Found: C, 72.36; H, 6.25.

4,4′,4″,4‴-[Silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedione), $Si(phprH)_4$ (6). A mixture of tetrakis(4-formylphenyl)silane (0.80 g, 1.78 mmol) and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene (3.20 g, 13.43 mmol) was stirred at room temperature under argon. After 20 h, 20 mL of methanol was added, and the mixture was refluxed under nitrogen for 3 h. During this time a white solid appeared, which was collected and dried under vacuum. Yield: 0.925 g (62%), mp 152−155 °C. ^{1}H NMR: δ 16.74 (s, 4H, O*H*); 7.57, 7.25 (m, 16H, aromatic C*H*); 2.14 (m, 16H, C*H*$_2$); 1.04 (m, 24H, C*H*$_3$). ^{13}C NMR: δ 194.2, 138.4, 136.1, 133.0, 130.4, 113.9, 30.2, 9.1. ^{29}Si NMR: δ 16.9. Anal. Calcd for $C_{52}H_{60}O_8Si$ (M = 841.11): C, 74.25; H, 7.19. Found: C, 73.89; H, 6.99.

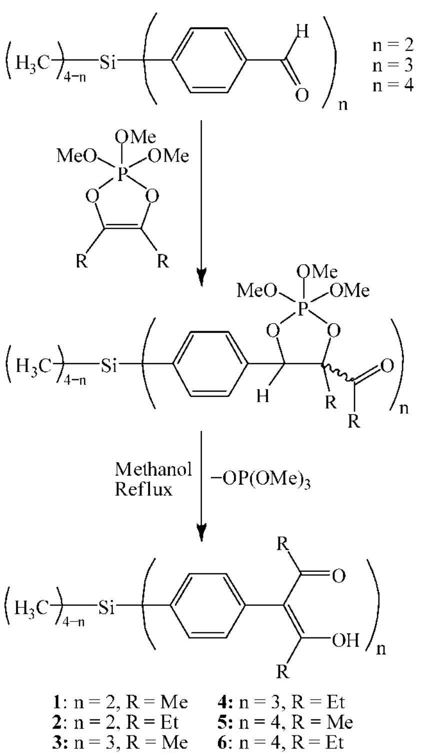
General Synthesis of the Complexes 7−18. The required $[M(COD)(\mu\text{-}Cl)]_2$ (M = Rh or Ir) (0.200 mmol) and a stoichiometric amount of β-diketone (chosen from **1**−**6**) were combined under N_2 in diethyl ether (20 mL), and aqueous KOH (1 mL, 1 M) was then added. The solution was stirred for 25−45 min. During this time a yellow solid precipitated. It was collected and washed with 2-propanol and pentane and dried. The crude product was recrystallized either from diethyl ether or a diethyl ether/$CHCl_3$ mixture.

Bis(1,5-cyclooctadiene)[μ-[3,3′-(dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedionato)]dirhodium, $(CH_3)_2Si(phacRh(COD))_2$ (7). Yield: 0.135 g (81%); dec 240 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*), 4.13 (s, 8H, =C*H*), 2.50 (m, 8H, C*H*$_2$), 1.87 (m, 8H, C*H*$_2$), 1.72 (s, 12H, C*H*$_3$), 0.55 (s, 6H,

Scheme 1. Synthesis of Aldehydes



Scheme 2. Synthesis of *β*-Diketones 1−6



Si*C*H_3). ^{13}C NMR: δ 185.8, 142.8, 136.4, 134.7, 131.2, 114.4, 76.8, 30.5, 28.6, −1.9. ^{29}Si NMR: δ 8.8. Anal. Calcd for $C_{40}H_{50}O_4Rh_2Si$ (M = 828.72): C, 57.97; H, 6.08. Found: C, 58.06; H, 5.96.

Bis(1,5-cyclooctadiene)[*μ*-[3,3′-[dimethylsilylenebis(1,4-phenylene)]bis(2,4-pentanedionato)]diiridium, $(CH_3)_2$Si(phac-Ir-(COD))$_2$ (8). Yield: 0.117 g (58%); dec 280 °C. ^{1}H NMR: δ 7.52, 7.13 (*AB*, 8H, aromatic C*H*), 4.04 (s, 8H, =C*H*), 2.31 (m, 8H, C*H*$_2$), 1.78 (s, 12H, C*H*$_3$), 1.70 (m, 8H, C*H*$_2$), 0.56 (s, 6H, SiC*H*$_3$). ^{13}C NMR: δ 185.7, 141.8, 136.9, 134.9, 131.0, 116.1, 59.9, 31.4, 28.6, −1.9. ^{29}Si NMR: δ 10.0. Anal. Calcd for $C_{40}H_{50}O_4Ir_2Si$ (M = 1007.30): C, 47.69; H, 5.00. Found: C, 47.90; H, 4.99.

Bis(1,5-cyclooctadiene)[*μ*-[4,4′-[dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedionato)]dirhodium, $(CH_3)_2$Si(phpr-Rh(COD))$_2$ (9). Yield: 0.135 g (76%); dec 198 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*); 4.13 (s, 8H, =C*H*), 2.50 (m, 8H, C*H*$_2$), 1.92 (m, 16H, C*H*$_2$ and C*H*$_2$CH$_3$); 0.85 (t, 12H, C*H*$_3$); 0.56 (s, 6H, SiC*H*$_3$). ^{13}C NMR: δ 188.6, 142.1, 135.7, 134.4, 131.6, 113.2, 76.9, 33.2, 30.5, 10.4, −2.6. ^{29}Si NMR: δ 13.8. Anal. Calcd for $C_{44}H_{58}O_4Rh_2Si$ (M = 884.83): C, 59.73; H, 6.61. Found: C, 59.52; H, 6.70.

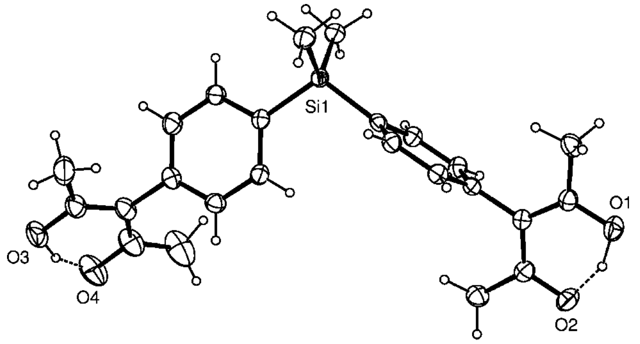


Figure 2. Molecular structure of $(CH_3)_2$Si(phacH)$_2$ (**1**) (ellipsoids shown at the 50% probability level).

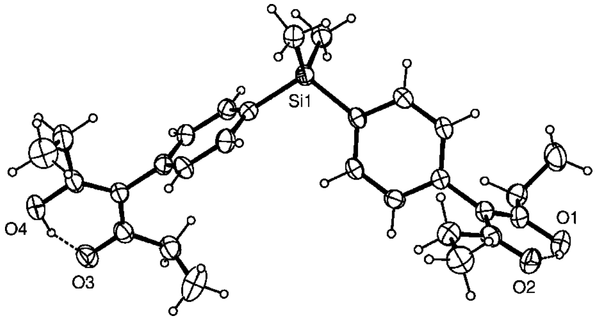


Figure 3. Molecular structure of $(CH_3)_2$Si(phprH)$_2$ (**2**) (ellipsoids shown at the 50% probability level). One of two crystallographically independent molecules in the asymmetric unit is shown.

Bis(1,5-cyclooctadiene)[*μ*-[4,4′-[dimethylsilylenebis(1,4-phenylene)]bis(3,5-heptanedionato)]diiridium, $(CH_3)_2$Si(phpr-Ir-(COD))$_2$ (10). Yield: 0.120 g (56%); dec 190 °C. ^{1}H NMR: δ 7.48, 7.12 (*AB*, 8H, aromatic C*H*; 4.04 (s, 8H, =C*H*), 2.31 (m, 8H, C*H*$_2$), 1.99 (q, 8H, C*H*$_2$CH$_3$), 1.70 (d, 8H, C*H*$_2$), 0.93 (t, 12H, C*H*$_3$); 0.57 (s, 6H, SiC*H*$_3$). ^{13}C NMR: δ 188.5, 141.3, 136.6, 135.1, 132.2, 115.0, 60.8, 33.3, 31.4, 10.9, −3.1. ^{29}Si NMR: δ 12.3. Anal. Calcd for $C_{44}H_{58}O_4Ir_2Si$ (M = 1063.45): C, 49.69; H, 5.50. Found: C, 49.90; H, 5.49.

Tris(1,5-cyclooctadiene)[*μ*-[3,3′,3″-[methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedionato)]trirhodium, CH_3Si(phac-Rh(COD))$_3$ (11). Yield: 0.147 g (92%); dec 288 °C. ^{1}H NMR: δ 7.46, 7.14 (*AB*, 12H, aromatic C*H*), 4.14 (s, 12H, =C*H*), 2.49 (m, 12H, C*H*$_2$), 1.87 (m, 12H, C*H*$_2$), 1.73 (s, 18H, C*H*$_3$), 0.83 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 185.7, 143.1, 135.8, 134.3, 131.3, 114.3, 76.8, 30.5, 28.6, −2.7. ^{29}Si NMR: δ 13.3. Anal. Calcd for $C_{58}H_{69}O_6Rh_3Si$ (M = 1198.97): C, 58.10; H, 5.80. Found: C, 57.92; H, 5.81.

Tris(1,5-cyclooctadiene)[*μ*-[3,3′,3″-[methylsilylidynetris(1,4-phenylene)]tris(2,4-pentanedionato)]triiridium, CH_3Si(phac-Ir-(COD))$_3$ (12). Yield: 0.141 g (72%); dec 276 °C. ^{1}H NMR: δ 7.50, 7.15 (*AB*, 12H, aromatic C*H*), 4.04 (s, 12H, =C*H*), 2.31 (m, 12H, C*H*$_2$), 1.80 (s, 18H, C*H*$_3$), 1.70 (m, 12H, C*H*$_2$), 0.85 (s, 3H, SiC*H*$_3$). ^{13}C NMR: δ 185.7, 142.2, 136.0, 134.8, 131.2, 116.1, 60.0, 31.4, 28.7, −2.7. ^{29}Si NMR: δ 13.6. Anal. Calcd for $C_{58}H_{69}Ir_3O_6Si$ (M = 1466.88): C, 47.49; H, 4.74. Found: C, 47.39; H, 4.70.

Tris(1,5-cyclooctadiene)[*μ*-[4,4′,4″-[methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedionato)]trirhodium, CH_3Si(phpr-Rh(COD))$_3$ (13). Yield: 0.164 g (95%); dec 220 °C. ^{1}H NMR: δ 7.47, 7.14 (*AB*, 12H, aromatic C*H*); 4.11 (s, 12H, =C*H*), 2.50 (m, 12H, CH_2), 1.92 (m, 24H, CH_2 and CH_2CH$_3$); 0.85 (m, 21H, CH_3 and SiCH_3). ^{13}C NMR: δ 188.6, 142.1, 135.7, 134.3, 131.6, 113.2, 76.8, 33.2, 30.5, 10.4, −2.6. ^{29}Si NMR: δ 12.6. Anal. Calcd for $C_{64}H_{81}Rh_3O_6Si$ (M = 1283.13): C, 59.91; H, 6.36. Found: C, 59.73; H, 6.33.

Tris(1,5-cyclooctadiene)[*μ*-[4,4′,4″-[methylsilylidynetris(1,4-phenylene)]tris(3,5-heptanedionato)]triiridium, CH$_3$Si(phpr-Ir-(COD))$_3$ (14). Yield: 0.141 g (68%); dec 290 °C. ^{1}H NMR: δ 7.51, 7.15 (*AB*, 12H, aromatic CH); 4.05 (s, 12H, =CH), 2.31 (m, 12H, CH_2), 2.00 (m, 12H, CH_2CH$_3$) 1.68 (m, 12H, CH_2); 0.91 (m, 21H, CH_3 and SiCH_3). ^{13}C NMR: δ 188.6, 136.7, 135.1, 132.3, 130.8, 115.0, 60.8, 33.4, 31.4, 11.0. ^{29}Si NMR: δ 13.0. Anal. Calcd for $C_{64}H_{81}Ir_3O_6Si$ (M = 1551.06): C, 49.56; H, 5.26. Found: C, 49.70; H, 5.49.

Tetrakis(1,5-cyclooctadiene)[*μ*-[3,3′,3″,3‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedionato)]tetrarhodium, Si(phac-Rh(COD))$_4$ (15). Yield: 0.071 g (45%); mp 168−174 °C. ^{1}H NMR: δ 7.51, 7.16 (*AB*, 16H, aromatic CH), 4.13 (s, 16H, =CH), 2.48 (m, 16H, CH_2), 1.88 (m, 16H, CH_2), 1.74 (s, 24H, CH_3). This compound was not sufficiently stable in CDCl$_3$ solution for recording a high-quality ^{13}C NMR spectrum. ^{29}Si NMR: δ 16.0. Anal. Calcd for $C_{76}H_{88}O_8Rh_4Si$ (M = 1569.21): C, 58.17; H, 5.65. Found: C, 57.88; H, 5.76.

Tetrakis(1,5-cyclooctadiene)[*μ*-[3,3′,3″,3‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(2,4-pentanedionato)]tetrairidium, Si(phac-Ir(COD))$_4$ (16). Yield: 0.113 g (58%). ^{1}H NMR: δ 7.55, 7.18 (*AB*, 16H, aromatic CH), 4.04 (s, 16H, =CH), 2.31 (m, 16H, CH_2), 1.82 (s, 24H, CH_3), 1.71 (m, 16H, CH_2). This compound was not sufficiently stable in CDCl$_3$ solution for recording high-quality ^{13}C or ^{29}Si NMR spectra. Anal. Calcd for $C_{76}H_{88}Ir_4O_8Si$ (M = 1926.46): C, 47.38; H, 4.60. Found: C, 47.01; H, 4.73.

Tetrakis(1,5-cyclooctadiene)[*μ*-[4,4′,4″,4‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedionato)]tetrarhodium, Si(phpr-Rh(COD))$_4$ (17). Yield: 0.148 g (88%); dec 246 °C. ^{1}H NMR: δ 7.52, 7.17 (*AB*, 16H, aromatic CH), 4.14 (s, 16H, =CH), 2.50 (m, 16H, CH_2), 2.00 (m, 16H, CH_2), 1.90 (q, 16H, CH_2CH$_3$), 0.86 (t, 24H, CH_3). ^{13}C NMR: δ 188.5, 142.5, 136.8, 132.6, 131.8, 113.2, 76.1, 33.2, 30.5, 10.4. ^{29}Si NMR: δ 17.2. Anal. Calcd for $C_{84}H_{104}O_8Rh_4Si$ (M = 1681.43): C, 60.00; H, 6.23. Found: C, 60.33; H, 6.45.

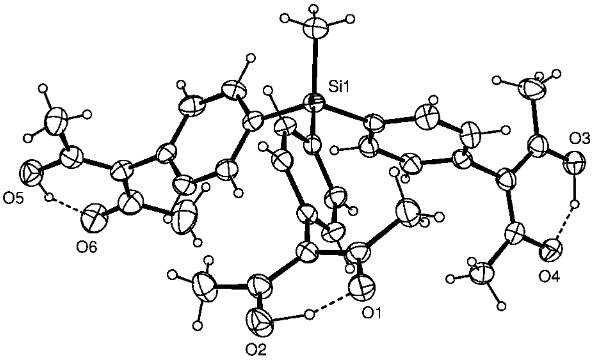


Figure 4. Molecular structure of CH$_3$Si(phacH)$_3$ (**3**) (ellipsoids shown at the 50% probability level).

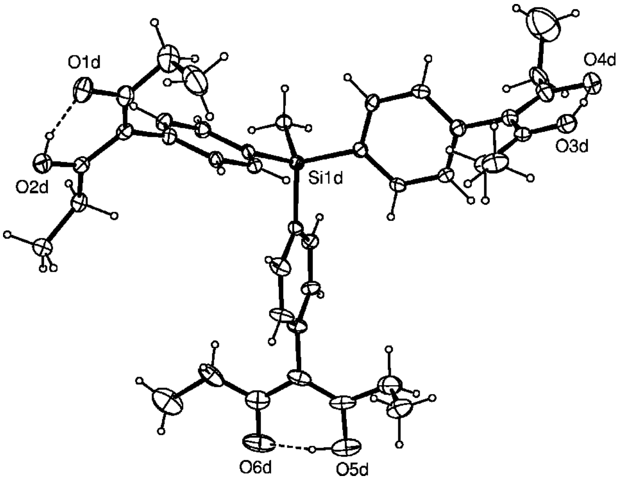


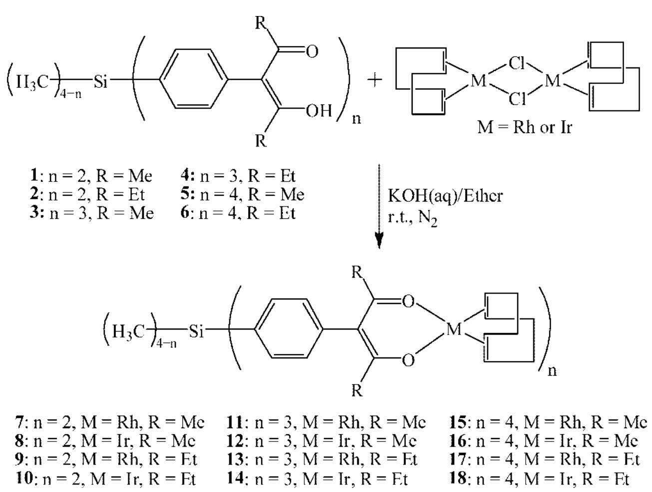
Figure 5. Molecular structure of CH$_3$Si(phprH)$_3$ (**4**) (ellipsoids shown at the 20% probability level). One of four crystallographically independent molecules in the asymmetric unit is shown.

Tetrakis(1,5-cyclooctadiene)[*μ*-[4,4′,4″,4‴-[silanetetrayltetrakis(1,4-phenylene)]tetrakis(3,5-heptanedionato)]tetrairidium, Si(phpr-Ir(COD))$_4$ (18). Yield: 0.108 g (53%); dec 204 °C. ^{1}H NMR: δ 7.53, 7.17 (*AB*, 16H, aromatic CH), 4.04 (s, 16H, =CH), 2.33 (m, 16H, CH_2), 2.04 (q, 16H, CH_2CH$_3$), 1.72 (m, 16H, CH_2), 0.93 (t, 24H, CH_3). ^{13}C NMR: δ 188.4, 141.6, 138.3, 136.9,

Table 1. Crystal Data and Structure Refinement for Multifunctional *β*-Diketones 1−4

	1	2	3	4
formula	$C_{24}H_{28}O_4Si$	$C_{28}H_{36}O_4Si$	$C_{34}H_{36}O_6Si$	$C_{40}H_{48}O_6Si$
fw	408.55	464.66	568.72	652.87
cryst size, mm	0.30 × 0.27 × 0.25	0.25 × 0.11 × 0.10	0.25 × 0.10 × 0.07	0.27 × 0.22 × 0.07
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	8.016(2)	9.845(2)	7.3493(10)	13.336(2)
b, Å	8.044(2)	16.663(3)	22.774(5)	22.955(3)
c, Å	17.791(4)	17.247(4)	18.640(5)	25.885(4)
α, deg	87.401(8)	68.294(10)	90	70.796(8)
β, deg	83.350(8)	89.725(8)	91.177(7)	78.854(8)
γ, deg	81.920(11)	83.072(9)	90	89.768(9)
V, Å^3	1127.7(5)	2607.1(10)	3119.2(12)	7326.8(18)
Z	2	4	4	8
D_{calc}, Mg/m^3	1.203	1.184	1.211	1.184
T, K	105	110	105	110
θ range, deg	2.5−27.9	2.5−24.4	2.5−27.5	2.5−23.0
μ, mm^{-1}	0.130	0.120	0.118	0.109
no. of measd reflns	33 395	16 020	59 143	86 197
no. of indep reflns	5394	8538	7145	20 205
no. of reflns $I > 2\sigma(I)$	4157	4921	3753	9984
no. of params	275	623	387	1726
goodness of fit	1.034	1.022	1.003	1.028
R ($I > 2\sigma(I)$)	0.042	0.060	0.056	0.095
wR_2	0.111	0.134	0.134	0.287
lgst diff, e Å^{-3}	0.29	0.22	0.30	0.93

Scheme 3. Synthesis of Rhodium(I) and Iridium(I) Complexes 7−18



131.6, 114.9, 60.0, 33.4, 30.2, 10.2. ^{29}Si NMR: δ 15.9. Anal. Calcd for $C_{84}H_{104}Ir_4O_8Si$ (M = 2038.67): C, 49.49; H, 5.14. Found: C, 49.25; H, 4.95.

X-ray Analyses. Single crystals suitable for X-ray analysis were obtained from methanol (**1**−**4**), chloroform (**7**), toluene (**11**), or diethyl ether (**13**). All X-ray data were collected on a Nonius KappaCCD instrument with Mo Kα source; crystals were mounted and then cooled to ca. 100 K in the gas stream from an Oxford Cryosystems Cryostream temperature-control device. Additional details concerning X-ray data collection and analysis are in the CIF file (see Supporting Information).

Results and Discussion

Multifunctional ligands with approximately tetrahedral angles between the ligand moieties can be derived from di-, tri-, and tetraphenylmethane. However, the Si analogues (i.e., di-, tri-, and tetraphenylsilanes; see Figure 1) are generally easier to synthesize, because of the availability of coupling reactions between aryllithium compounds and chlorosilanes.[11−22] Thus, tetraphenylsilane is considerably easier to prepare than tetraphenylmethane. Still, even among the oligoarylsilanes, some derivatives have presented synthetic challenges: for example, Wuest et al. reported that tetrakis(4-formylphenyl)silane was difficult to prepare in pure form.[11] We recently used[9] the method of Ramirez et al.[23−25] to prepare new aromatic bis(β-diketones) from the analogous aldehydes. For the present work, we wished to prepare a family of bis-, tris-, and tetrakis(β-diketones) with approximately tetrahedral angles, for reaction with metal ions. To do this, we needed the corresponding di-, tri-, and tetraaldehydes (i.e., bis-, tris-, and tetrakis(formylphenyl)silanes) as starting materials.

Synthesis of Aldehydes. Lithiation of 4-bromobenzaldehyde dimethyl acetal, followed by treatment with $(CH_3)_2SiCl_2$, produces a bis(acetal) that yields bis(4-formylphenyl)dimethylsilane ($(CH_3)_2Si(4\text{-}C_6H_4CHO)_2$) on hydrolysis.[10] We carried out analogous reactions with CH_3SiCl_3 and $SiCl_4$ and obtained the other needed aldehydes, tris(4-formylphenyl)methylsilane ($CH_3Si(4\text{-}C_6H_4CHO)_3$, liquid) and tetrakis(4-formylphenyl)silane ($Si(4\text{-}C_6H_4CHO)_4$, crystalline solid). This synthesis is summarized in Scheme 1.

Synthesis of β-Diketones. The aldehydes prepared here react with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene or 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene at ambient temperature under N_2 to produce dioxaphospholanes, which on refluxing in methanol yield the new β-diketones (**1**−**6**), as shown in Scheme 2. These compounds contain either two ($Me_2Si(phacH)_2$, **1**; $Me_2Si(phprH)_2$, **2**), three ($MeSi(phacH)_3$, **3**; $MeSi(phprH)_3$, **4**), or four ($Si(phacH)_4$, **5**; $Si(phprH)_4$, **6**) β-diketone substituents; in the abbreviations, "ac" and "pr" represent the β-diketone moieties acetylacetone and dipropionylmethane (3,5-heptanedione), respectively.

Crystal Structure Analyses of β-Diketones. Compounds **1**−**4** were also structurally characterized by single-crystal X-ray diffraction. Selected data from these studies are given in Table 1. ORTEP diagrams for **1**−**4** are shown in Figures 2−5.

All of the β-diketones **1**−**4** are in the enol form in their crystals, in agreement with the results of ^{1}H NMR spectral measurements in solution. In all of these structures, the refined positions for the enol H atoms are closer to one O atom than the other, and there is also slight alternation of bond lengths in

Table 2. Crystal Data and Structure Refinement for Rh Complexes 7, 11, and 13

	7·$2CHCl_3$	**11**·C_7H_8	**13**·Et_2O
formula	$C_{40}H_{50}O_4Rh_2Si\cdot 2CHCl_3$	$C_{58}H_{69}O_6Rh_3Si\cdot C_7H_8$	$C_{64}H_{81}O_6Rh_3Si\cdot Et_2O$
fw	1067.45	1291.09	1357.23
cryst size, mm	0.30 × 0.20 × 0.12	0.35 × 0.04 × 0.03	0.40 × 0.22 × 0.10
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	13.507(1)	6.8596(10)	7.1909(15)
b, Å	15.562(1)	16.044(3)	16.858(2)
c, Å	22.7090(15)	27.200(5)	25.998(3)
α, deg	70.463(4)	98.156(7)	85.689(4)
β, deg	86.892(3)	96.646(9)	84.728(4)
γ, deg	87.139(3)	97.498(9)	84.439(4)
V, Å^3	4489.3(5)	2910.3(9)	3116.5(8)
Z	4	2	2
D_{calc}, Mg/m^3	1.579	1.473	1.446
T, K	100	90	90
θ range, deg	2.6−30.0	2.5−25.0	2.5−28.7
μ, mm^{-1}	1.159	0.912	0.856
no. of measd reflns	41 327	34 484	109 435
no. of indep reflns	26 062	10 169	15 301
no. of reflns $I > 2\sigma(I)$	14 921	6446	11 670
no. of params	1018	639	776
goodness of fit	0.977	1.022	1.028
R ($I > 2\sigma(I)$)	0.052	0.060	0.061
wR_2	0.142	0.138	0.152
lgst diff, e Å^{-3}	1.75	1.01	2.55

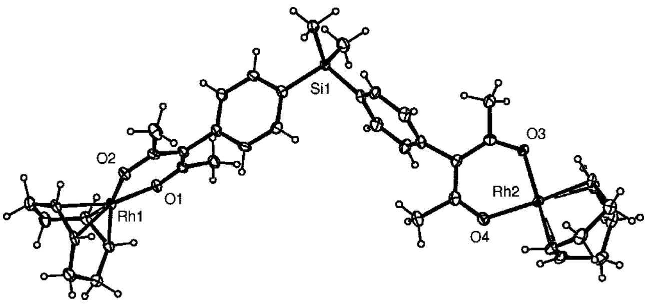


Figure 6. Molecular structure of $(CH_3)_2Si(phac\text{-}Rh(COD))_2$ (**7**) (ellipsoids shown at the 50% probability level). One of two crystallographically independent molecules in the asymmetric unit is shown. Selected interatomic distances (Å): Rh1−O1 2.042(2); Rh1−O2 2.040(3); Rh2−O3 2.025(2); Rh2−O4 2.031(3).

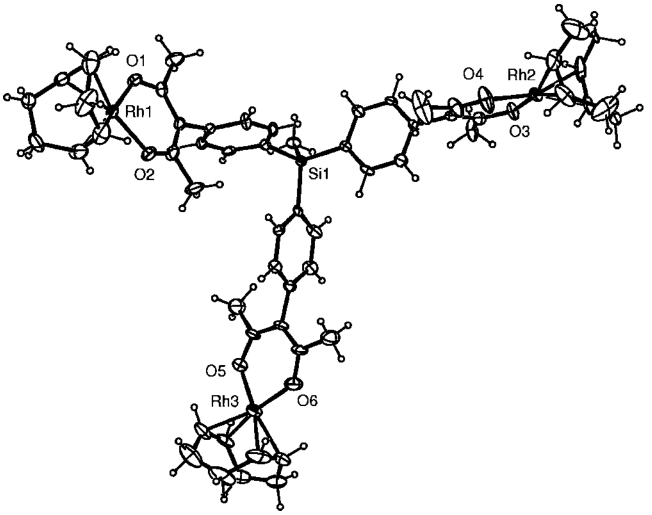


Figure 7. Molecular structure of $CH_3Si(phac\text{-}Rh(COD))_3$ (**11**) (ellipsoids shown at the 50% probability level). Selected interatomic distances (Å): Rh1−O1 2.040(5); Rh1−O2 2.038(5); Rh2−O3 2.043(4); Rh2−O4 2.031(5); Rh3−O5 2.020(5); Rh3−O6 2.029(5).

the O−C−C−C−O chelate rings. Only intramolecular O−H···O hydrogen bonds, and no unusual intermolecular contacts, were observed in these structures.

A search of the Cambridge Structural Database[26] [database version 5.29, updated to November 2007] revealed 13 compounds in which one or more β-diketone moieties are directly attached to aromatic rings.[27] Like the present compounds, all of the previous examples are in the enol form. Enolic β-diketones typically show some alternation among C−O and C−C bond lengths around the rings: average values for all structures (including those reported here) are C−O, 1.321 ± 0.019; C−C, 1.383 ± 0.012; C−C, 1.425 ± 0.019; and C−O, 1.274 ± 0.015 Å. These values represent relatively small differences in length between the formal single and double bonds of the enol structure. This effect has been discussed in terms of resonance-assisted hydrogen bonding: for β-diketones in the enol form, which have O···O distances between 2.4 and 2.5 Å, the strength of the OH···O hydrogen bond and the resulting amount of resonance are large, leading to a high degree of delocalization and a small amount of bond length alternation.[28,29]

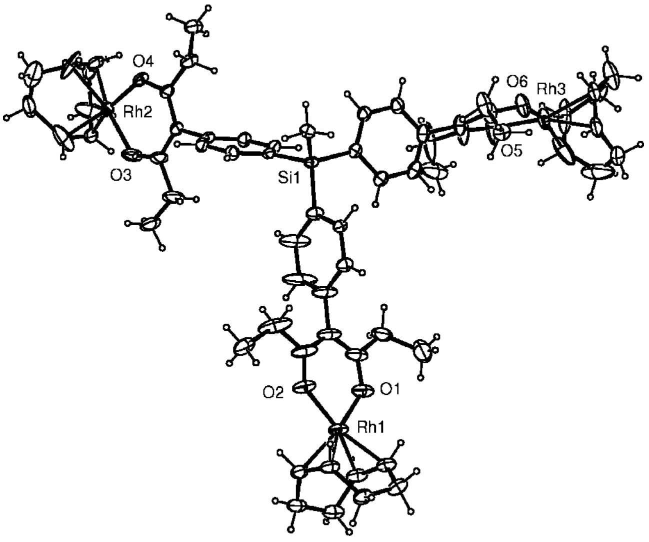


Figure 8. Molecular structure of $CH_3Si(phpr\text{-}Rh(COD))_3$ (**13**) (ellipsoids shown at the 40% probability level). Selected interatomic distances (Å): Rh1−O1 2.032(4); Rh1−O2 2.042(4); Rh2−O3 2.013(4); Rh2−O4 2.026(3); Rh3−O5 2.032(4); Rh3−O6 2.033(4).

Rhodium(I) and Iridium(I) Complexes. Early preparations of (acac)M(COD) were reported by Chatt and Venanzi[30] and by Bonati and Wilkinson[31] (M = Rh), and by Platzer et al.[32] (M = Ir). The reaction of $[M(COD)(\mu\text{-}Cl)]_2$ (M = Rh and Ir) with simple bis(β-diketones) to form binuclear complexes was reported by Whitmore and Eisenberg.[33] (Among more recent studies of related complexes is that of Tokitoh et al., who

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Table 3. Selected Distances (Å) and Angles (deg) for Compounds 1−4, 7, 11, and 13

	1	2	3	4		7	11	13
Oc[a]···Si	8.221	8.216	8.221	8.224	8.223			
	8.234	8.224	8.219	8.196	8.241			
			8.221	8.229	8.196			
		8.216						
		8.225		8.216	8.217			
				8.217	8.212			
				8.189	8.230			
Oc···Oc	13.667	13.684	13.027	13.072	13.173			
		13.407	13.065	13.999	13.751			
			13.080	13.349	13.096			
				13.591	13.498			
				13.393	13.141			
				13.068	13.340			
Si···Rh						9.5717(12)	9.541(3)	9.563(2)
						9.5242(13)	9.556(3)	9.577(2)
							9.575(3)	9.594(2)
						9.5586(12)		
						9.5759(13)		
Rh···Rh						16.0281(9)	13.889(2)	14.661(2)
						16.2330(9)	15.591(2)	16.015(2)
							16.098(3)	16.088(2)
Oc···Si···Oc	112.3	112.68	104.82	111.77	105.49			
		109.27	105.26	105.52	109.14			
			105.41	108.74	111.28			
				106.57	110.49			
				113.90	108.41			
				105.93	106.11			
Rh···Si···Rh						113.79(1)	93.32(2)	99.99(1)
						116.44(1)	109.30(2)	113.44(2)
							114.58(2)	114.11(1)

[a] "Oc" = O centroid of β-diketones.

prepared Rh β-ketophosphenates and β-ketoiminates.[34]) We used a similar procedure to prepare Rh and Ir complexes of the new silicon-based multifunctional β-diketones. Compounds **1**−**6** react with [M(COD)(μ-Cl)]$_2$ (M = Rh and Ir) in the presence of added base to form multimetallic silicon-bridged Rh and Ir complexes (Scheme 3, which are soluble in common organic solvents. The spectral properties of the new multinuclear metal complexes are similar to those of the simpler Rh and Ir complexes, with (for example) both aromatic and aliphatic ^{1}H resonances showing slight upfield shifts compared to the uncomplexed β-diketones.

Crystal Structure Analyses of Rhodium Complexes. Compounds **7**, **11**, and **13** were also structurally characterized by single-crystal X-ray diffraction; see summary in Table 2). The molecular structures of **7**, **11**, and **13** are shown in Figures 6, 7, and 8.

The structures of the (diketonato)Rh(COD) moieties in these crystals are similar to those in six previously published structures.[35] In the COD moieties in the present structures, the C=C bonds are not quite perpendicular to the Rh−diketonate plane: in each case, both are twisted away from perpendicularity in the same direction. This situation is also found in all of the previously published (diketonato)Rh(COD) and (diketonato)Ir(COD) structures, and it is likely due to the fact that the most stable conformation of the COD molecule itself is similarly twisted. No unusual intermolecular contacts were observed in these structures.

Intramolecular distances and angles involving the Si atoms, the Rh atoms, and the β-diketone O atom centroids ("Oc"), as derived from the X-ray analyses, are presented in Table 3. These values show that the β-diketone moieties in **1**−**4** are ca. 13.3 Å apart, and the Rh···Rh distances in the complexes are ca. 15.6 Å. The complexes can also be viewed as composed of "rods" ca. 9.56 Å long (Si···Rh) that make approximately tetrahedral angles at Si (average 109.4°). These data will assist in designing and synthesizing supramolecular structures with arylsilane-based building blocks.

Conclusions

The aim of this study was to prepare multifunctional β-diketones and to investigate their coordination properties. Hence, we have developed a simple method for the synthesis of new organosilicon-based tri- and tetraaldehydes as well as bis-, tris-, and tetrakis(β-diketones). The simple, general, clean, and convenient method presented here has led to desirable tetrahedral building blocks for metal-organic frameworks. Crystal structure analyses were performed for β-diketones **1**−**4** and for three of their polynuclear Rh complexes (**7**, **11**, and **13**). At present, we are exploring the reactivity of the polytopic β-diketones **1**−**6** with other metal salts.

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Supporting Information Available: X-ray crystallography data for **1**−**4**, **7**, **11**, and **13** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[35] Refcodes: BFACRH ((benzoyltrifluoroacetonato)Rh(COD)); COCACR ((acac)Rh(COD)); LABLIJ ((ferrocenyl-1,3-butanedionato)Rh(COD)); LEVCEU ((trifluoroacetylacetonato)Rh(COD)); QOZZAG ((hexafluoroacetylacetonato)Ir(COD)).