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Highly Soluble Penta[(alkyl)dimethylsilylmethyl][60]fullerenes and Their Ruthenium and Palladium Complexes

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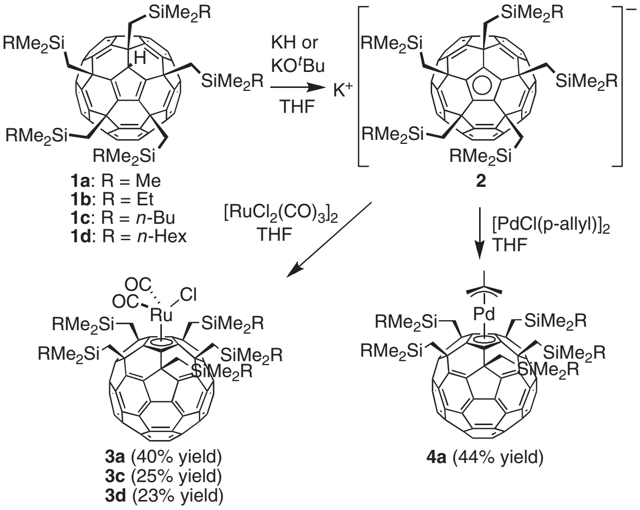
Copper-mediated fivefold addition of RMe_2SiCH_2MgCl to [60]fullerene produces $C_{60}(CH_2SiMe_2R)_5H$ ($R = H$, Et, *n*-Bu, and *n*-hexyl), which can be further converted into ruthenium and palladium complexes. These organofullerenes and metal–fullerene complexes, particularly when $R = n$-Hex, are highly soluble in various organic solvents, e.g., $107\,mg\,mL^{-1}$ solubility in EtOAc and $>1000\,mg\,mL^{-1}$ in hexane, where $C_{60}Me_5H$ is essentially insoluble.

The low solubility of fullerene in a variety of solvents[1] often poses problems in practical applications. This is one of the reasons why organic derivatives of fullerene are indispensable in fullerene research, including the hot area of organic photovoltaics.[2] Inorganic chemistry of fullerene being no exception, we have expended considerable effort to make soluble organometallic derivatives, for instance, η^5-organometallic complexes of penta(organo)[60]fullerenes[3] ($M[C_{60}R_5]$) where R includes aryl, alkenyl, and methyl groups. The pentaaryl derivatives have been utilized effectively for the development of new liquid crystals,[4] vesicles,[5] and photocurrent generation systems.[6] The pentamethyl derivatives[3b,3c] were utilized in the synthesis of a variety of transition-metal complexes,[3d,7] but $C_{60}Me_5H$ and the metal complexes are often sparingly soluble, e.g., $<10\,mg\,mL^{-1}$, in solvents commonly used for catalysis or materials applications. Herein we report the use of five RMe_2SiCH_2 groups for the preparation of highly soluble metal complexes, as illustrated by the synthesis of ruthenium and palladium complexes of penta(dimethylalkylsilylmethyl)[60]fullerene, $C_{60}(CH_2SiMe_2R)_5H$ (R = Me (**1a**), Et (**1b**), *n*-Bu (**1c**), and *n*-hexyl (**1d**)). The aliphatic chains attached to the silicon atom endow these metal complexes with good solubility but do not have much effect on the coordination environment as they are located far from the metal center. The present results corroborate our recent observation that the RMe_2SiCH_2 groups in bis(silylmethyl)fullerenes ($C_{60}(CH_2SiMe_2R)_2$) can control the solubility and thermal properties without much affecting the electronic properties of the fullerene core.[8]

The synthesis utilizes a copper-mediated pentaaddition of RMe_2SiCH_2MgCl to [60]fullerene (Scheme 1), which was found to require conditions slightly different from that developed previously for the pentaaddition of aryl and methyl Grignard reagents.[3b] Thus, we added a solution of C_{60} in *ortho*-dichlorobenzene to a suspension of the organocopper reagent prepared from the reaction of RMe_2SiCH_2MgCl (16 equiv) with $CuBr{\cdot}SMe_2$ (18 equiv) in the mandatory presence of *N*,*N′*-dimethylimidazolidinone (18 equiv) at 0 °C and subsequent stirring at 25 °C. The reaction afforded **1a** (R = Me) in 75% yield as a reddish-brown solid, **1b** (R = Et) in 79% yield and **1c** (R = *n*-Bu) in 87% yield. The reaction in which R = *n*-Hex also took place smoothly but gave **1d** in 28% isolated yield because of the difficulty of separating a homocoupling product of the Grignard reagent using silica gel chromatography. These products are stable in air in the solid state but degrade slowly in solution to oxygenated products.[9]



Scheme 1.

Compound **1a** was characterized by high-resolution APCI-TOF MS, and ^1H and ^{13}C NMR spectroscopy as well as single-crystal X-ray analysis of the corresponding ruthenium complex (see below). The ^1H NMR signals due to the five methylene groups appeared as four doublet signals at δ 1.85, 1.90, 2.00, and 2.11 with geminal coupling ($^2J_{H\text{–}H} \approx 14.4\,Hz$) and a singlet signal at δ 2.15, indicating that **1a** is C_s symmetric. The signal of the hydrogen atom directly attached to the fullerene core appeared at δ 4.57 (in $CDCl_3$), which is similar to $C_{60}Me_5H$ (δ 4.42) but at higher field than the signal of $C_{60}Ph_5H$ (δ 5.30).

Deprotonation of **1a** with KH in THF generated a black solution of the corresponding potassium cyclopentadienide, $[K(thf)_n][C_{60}(CH_2SiMe_3)_5]$ (**2a**).[10] The ^1H and ^{13}C NMR spectra of **2a** in THF-d_8 indicate that the anion is C_{5v}-symmetric: the ^1H NMR showed only two proton signals at δ 0.27 (CH_3) and 2.44 (CH_2). The ^{13}C NMR signal assigned to the cyclopentadienyl carbon atoms appeared at slightly lower field (δ 131.86) than those of $[K][C_{60}Me_5]$ (δ 129.70) and $[K][C_{60}Ph_5]$ (δ 128.85), suggesting that a certain degree of electronic effect is exerted by the Me_3Si group located two σ bonds away from the cyclopentadienide moiety.

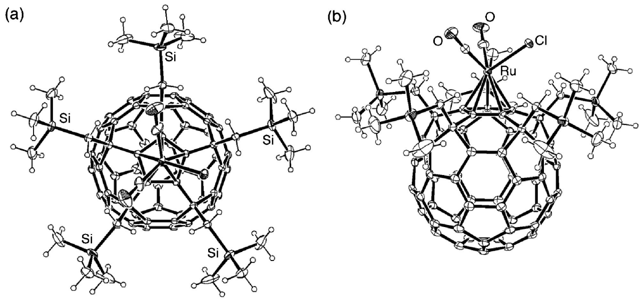


Figure 1. Molecular structure of **3a**.

The potassium complex **2a** was converted to transition-metal complexes. Treatment of **2a** with $[RuCl_2(CO)_3]_2$[7a] in THF produced a ruthenium(II) complex, $Ru[C_{60}(CH_2SiMe_3)_5]Cl(CO)_2$ (**3a**), as air-stable reddish-orange crystals in 40% yield. The ruthenium(II) complexes **3c** and **3d** bearing *n*-butyl and *n*-hexyl groups were also synthesized in a similar manner. Note that we have so far been unable to synthesize the corresponding $C_{60}Ar_5$ complexes, probably because of the steric bulk of the five aryl groups. Similarly, the reaction with $[Pd(methallyl)Cl]_2$[7b] in THF afforded a palladium(II) complex, $Pd[C_{60}(CH_2SiMe_3)_5](\eta^3\text{-}C_4H_7)$ (**4a**), as red crystals in 45% yield.

The ^1H NMR spectrum of **3a** displayed two singlet signals at δ 0.11 (CH_3) and 2.19 (CH_2), indicating that the $C_{60}(CH_2SiMe_3)_5$ ligand is C_{5v}-symmetric in the NMR timescale. The carbonyl ligand on the metal center appeared at δ 196.73 in the ^{13}C NMR spectrum, and at $\nu_{asym}(CO) = 2050\,cm^{-1}$ and $\nu_{asym}(CO) = 1999\,cm^{-1}$ in the IR spectrum. The IR wavenumbers are smaller than those of $Ru(C_{60}Me_5)Cl(CO)_2$ (2059 and 2008 cm^{-1}),[7a] suggesting that the $C_{60}(CH_2SiMe_3)_5$ ligand is more electron rich than the $C_{60}Me_5$ ligand.[3b]

Recrystallization of **3a** from chloroform/methanol afforded a single crystal suitable for X-ray crystallographic analysis; ORTEP figures are shown in Figure 1. The average interatomic distance (2.27 Å) between the ruthenium atom and the η^5-cyclopentadienyl carbon atoms in **3a** is comparable to that found for $Ru(C_{60}Me_5)Cl(CO)_2$ (average distance of 2.27 Å),[7a] and there appears to be little steric congestion between the ruthenium metal and five methylene groups, as suggested by visual analysis of a CPK model. On the basis of this crystal structure of **3a**, we surmise that the alkyl groups in **3b** and **3c** would be located far from the metal center, rotate freely, and contribute to the increased solubility of the metal complex.

The solubility of penta(organo)[60]fullerenes **1a**, **1c**, and **1d** and their ruthenium complexes **3a**, **3c**, and **3d** in common organic solvents was determined with the aid of UV measurements[11] (Table 1). Solubility higher than 10 mg mL^{-1} may be desirable for these metal complexes to be utilized for catalytic applications, but the metal $C_{60}Me_5$ complexes we have synthesized thus far did not always meet this criterion. For instance, $C_{60}Me_5H$ is hardly soluble in any of the solvents shown in Table 1. We found that the Me_3SiCH_2 groups already allow **1a** to acquire solubility higher than 10 mg mL^{-1} in THF, chloroform, and toluene, and the solubility of $C_{60}(BuMe_2SiCH_2)_5H$ (**1d**) exceeds 22 mg mL^{-1} even in hexane. The solubility of the ruthenium complexes **3** is uniformly higher than that of the fullerene ligand **1**, and that of $C_{60}(EtMe_2SiCH_2)_5$ ruthenium complex **3c** approaches 200 mg mL^{-1}. The $C_{60}(BuMe_2SiCH_2)_5$ ruthenium complex **3d**, which is viscous oil by itself, is freely miscible with hexane, and when 1 g is dissolved in 1 mL of hexane forms a mesophase as revealed by polarizing optical microscopy.[4]

Table 1. Solubility (mg mL^{-1}) of $C_{60}(CH_2SiMe_2R)_5H$ (R = Me, *n*-Bu, and *n*-Hex) and their ruthenium complexes

	1a	**1c**	**1d**	**3a**	**3c**	**3d**
Hexane	0.77	5.38	22.3	8.21	184	>1000
EtOAc	—	1.16	1.27	10.4	11.1	107
THF	10.8	—	—	82.5	—	—
$CHCl_3$	11.5	—	—	56.2	—	—
Toluene	5.62	—	—	14.9	—	—

In conclusion, we have developed a highly soluble surrogate of the $C_{60}Me_5$ ligand through the use of flexible (alkyl)dimethylsilylmethyl addends installed on the [60]fullerene core. The X-ray structure suggests that the metal coordination sphere in the immediate vicinity of the metal is quite open and hence that these soluble metal complex will be amenable to use in catalysis and materials research.

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11 Several solutions of each compound in hexane with known concentrations were prepared. UV absorptions were measured to make a standard line; the intensities of the absorption at λ_{max} near 355 nm were plotted for the concentrations. A saturated solution of the compound was prepared by filtration through membrane filter (0.2 μm) after stirring a suspension of it in a solvent. The saturated solution was diluted with several hundred times of hexane and measured UV absorption to determine the concentration.