

# Direct Synthesis of $\eta^6$ -1-Functionally Substituted 2,3,4,5-Tetraphenyl-1-Silacyclopentadiene Complexes of Chromium

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We synthesized the novel complexes of (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-ylidibenzene)bis(tricarbonylchromium) and tricarbonyl (R,R'-3,4,5-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene)chromium (R,R' = Me, R = Me/R' = Cl, R = Ph/R' = Cl) from the reaction of the corresponding R,R'-2,3,4,5-Tetraphenyl-1-silacyclopenta-2,4-diene (abr. R,R'-TPSCp) with chromiumhexacarbonyl. These results reveal that chromium prefer to coordinate to the phenyl substituents of 1-silacyclopentadiene rather than the butadiene moiety of the ring.

## Introduction

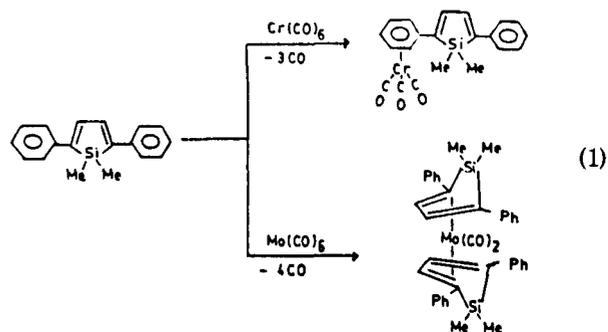
A great number of investigations has focused on the synthesis of 1-silacyclopentadiene  $\eta^4$ -complexes of transition metals because it has been of interest whether  $\eta^4$ -1-silacyclopentadiene complexes will be converted to  $\eta^5$ -1-silacyclopentadienyl complexes. Still unreported, however, is the generation or detection of such  $\eta^4$ -complexes except mass spectrometric studies<sup>1,2</sup>.

Metalcarbonyl complexes of 1,1-diorgano-1-silacyclopentadiene<sup>3,4</sup>, 1,1-diorgano-3,4-dimethyl-1-silacyclopentadiene<sup>5-8</sup>, and 1,1-diorgano-2,5-diphenyl-1-silacyclopentadiene<sup>9-13</sup> have been studied extensively. These metal complexes have been restricted to those of iron, cobalt, nickel, molybdenum, and tungsten. All of them are  $\eta^4$ -complexes formed through the butadiene moiety of 1-silacyclopentadiene with carbonyls of iron, cobalt, nickel, molybdenum, tungsten. However, the chromium complexes of 1-silacyclopentadiene are scarcely known. On the other hand, studies for the metal carbonyl complexes of 1-functionally substituted 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (R, R'-TPSCp) are also scarce in literature<sup>14-16</sup>. Previously, we reported that 1-functionally substituted 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene are so reactive to form new  $\eta^4$ -complexes of ironpentacarbonyl directly under mild reaction conditions.<sup>14</sup>

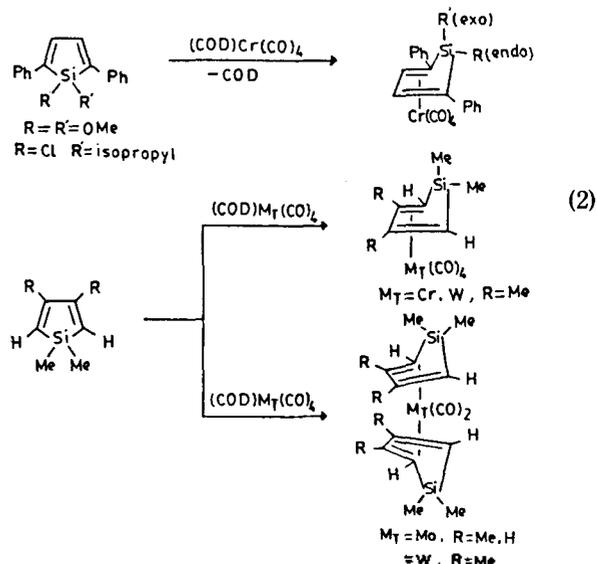
In this respect, we have studied the complexation of chromium with 1-functionally substituted R,R'-TPSCp (R = R' = Me, R = Me/R' = Cl, R = Ph/R' = Cl) and synthesized several new  $\eta^6$ -complexes of chromium.

## Results and Discussion

It was reported that the reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with chromiumhexacarbonyl led to  $\eta^6$ -complexes of tricarbonyl (1,1-dimethyl-5-phenyl-1-silacyclopentadiene-2-ylbenzene) chromium. Whereas, with molybdenumhexacarbonyl,  $\eta^4$ -complexes of dicarbonyl bis(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene) molybdenum was formed. From these results, chromium may prefer to form rather  $\eta^6$ -complex with arene than  $\eta^4$ -complex with diene moiety, whereas the molybdenum behaves in the reverse ways<sup>10</sup>.

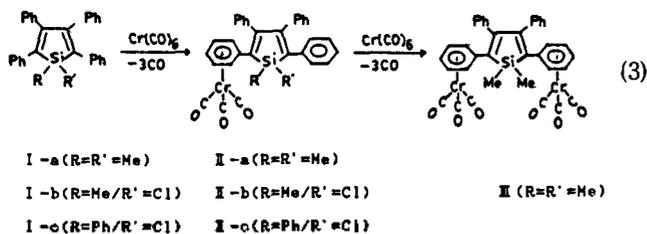


In contrast, the reaction of  $(\text{COD})\text{Cr}(\text{CO})_4$  with 1,1,3,4-tetramethyl-1-silacyclopentadiene<sup>7</sup>, and 1,1-diorgano-2,5-diphenyl-1-silacyclopentadiene<sup>18</sup> were reported to give  $\eta^4$ -complexes of tetracarbonyl (1-silacyclopentadiene) chromium. Whereas, in the reaction of  $(\text{COD})\text{Mo}(\text{CO})_4$  with 1,1-dimethyl-1-silacyclopentadiene, and 1,1,3,4-tetramethyl-1-silacyclopentadiene, all complexation led to dicarbonyl-bis(1-silacyclopentadiene) molybdenum like distorted sandwich compound, and the reaction of  $(\text{COD})\text{W}(\text{CO})_4$  with 1,1,3,4-tetramethyl-1-silacyclopentadiene led to both tetracarbonyl(1,1,3,4-tetramethyl-1-silacyclopentadiene) tungsten and dicarbonylbis(1,1,3,4-tetramethyl-1-silacyclopentadiene) tungsten<sup>7</sup>.

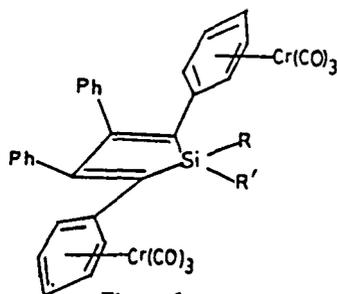


From these results, it was indicated that chromium would not only be able to form  $\eta^4$ -complex from ligand exchange reaction but also be able to form  $\eta^6$ -complex from direct complexation reaction. However, it is somewhat unexpected result that only one phenyl substituent of two does coordinate to chromium, although the ligand of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene has a vertical mirror plane.

In our work, the novel complexes of (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-ylidibenzene)-bis(tricarbonylchromium) (III) and tricarbonyl(1,1-dimethyl-3,4,5-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene) chromium (II-a) were obtained from the reaction of  $\text{Cr}(\text{CO})_6$  with  $\text{R,R}'\text{-TPSCp}(\text{R}=\text{R}'=\text{Me})$ . The complex of III was also obtained from the reaction of II-a with chromiumhexacarbonyl. On the other hand, from the reaction of 1-functionally substituted  $\text{R,R}'\text{-TPSCp}(\text{R}=\text{Me}/\text{R}'=\text{Cl}, \text{R}=\text{Ph}/\text{R}'=\text{Cl})$  with chromiumhexacarbonyl, we isolated  $\eta^6$ -complexes of II-b, II-c, respectively.



These novel complexes might have geometric isomers of two, because phenyl substituents of ligand  $\text{R,R}'\text{-TPSCp}$  could not rotate due to the crowding of four bulky phenyl substituents. In fact, by the analysis of the structure of  $\text{Fe}[\text{R,R}'\text{-TPSCp}(\text{CO})_3] (\text{R}=\text{Ph}/\text{R}'=\text{Cl})$  the rotation of phenyl is not possible<sup>17</sup>. The chemical shifts of II-a, III and II-b in  $^1\text{H-NMR}$  were observed at 0.67, 0.86 and 1.12 ppm for methyl group as singlet, respectively. These chemical shift values were more deshielded than 0.47 ppm of ligand (I-a) and 0.86 ppm of ligand (I-b), each chemical shift differences of complex and its ligand were 0.20(II-a), 0.39(III) and 0.26(II-b) ppm. Therefore, it was supposed that the plane of  $\eta^6$ -Phenyl ring was located vertical to the plane of butadiene moiety of ligand (Figure 1.), this made the chemical surroundings of methyl groups equal and such lower field shifts were due to the reduced electron density of Si-Me by the electron withdrawing of chromiumtricarbonyl through the arene ring.



From these results, we conclude that chromium prefer to coordinate to the phenyl substituents of these  $\text{R,R}'\text{-TPSCp}(\text{R}=\text{R}'=\text{Me}, \text{R}=\text{Me}/\text{R}'=\text{Cl}, \text{R}=\text{Ph}/\text{R}'=\text{Cl})$  rather than the butadiene moiety of the ring, the complexation of III

may probably proceed *via* II-a followed by the additional complexation with chromiumhexacarbonyl.

## Experiments

All reactions were routinely carried out under an atmosphere of nitrogen using anhydrous solvents. Elemental analyses were performed by Yanaco, MT-2 Elemental analyzer at the Chemical analytic Center of the college of Engineering, Seoul National University.  $^1\text{H-NMR}$  Spectra were obtained on Bruker WP 80 SY, 80 MHz FT-NMR, Mass spectra on Jeon Gas-Chromatography and Mass Spectrometer DMX 300, IR as KBr-pellet on Shimadzu IR-440 and Melting point on Wagner & Műnz, Co., Capillary type.

$\text{R,R}'\text{-TPSCp}(\text{R}=\text{R}'=\text{Me}, \text{R}=\text{Me}/\text{R}'=\text{Cl}, \text{R}=\text{Ph}/\text{R}'=\text{Cl})$ . These compound were prepared according to the procedure improved by us<sup>17</sup>. 105 mmol of  $\text{R}_n\text{SiCl}_{4-n}$  was added at the temperature of liquid nitrogen to 120 ml of diethylether suspension of 1,4-dithio-tetraphenylbutadiene obtained from 10.7g(60 mmol) of diphenylacetylene and 0.5g (71mg atom) of lithium. The reaction mixture was allowed to warm to room temperature with stirring vigorously for three hours. The greenish-yellow solution was separated from the precipitate by decantation. The residue was extracted by adding 100 ml of diethylether two or three times. After the solution thus obtained was concentrated to an half of its volume, and was kept at  $-20^\circ\text{C}$  for one day. Greenish-yellow crystals of  $\text{R,R}'\text{-TPSCp}(\text{R}=\text{R}'=\text{Me}, \text{R}=\text{Me}/\text{R}'=\text{Cl}, \text{R}=\text{Ph}/\text{R}'=\text{Cl})$  were obtained.

$\text{R,R}'\text{-TPSCp}(\text{R}=\text{R}'=\text{Me})$  (I-a); mp.  $181^\circ\text{C}$ (lit.<sup>19</sup>  $181\text{--}182^\circ\text{C}$ ), Anal. Calcd. (found) for  $\text{C}_{30}\text{H}_{26}\text{Si}$ , C, 86.91 (85.70), H, 6.32(6.24), mass *m/e* 414( $\text{M}^+$ ), 399( $\text{M}^+-\text{Me}$ ),  $^1\text{H-NMR}(\text{CDCl}_3, \text{ppm})$ , 0.47(s, 6H, SiMe), 6.7-7.2 (brd.m, 2OH, Ph),  $^{13}\text{C-NMR}(\text{CDCl}_3, \text{ppm})$ , -3.92 (SiMe), 154.01(C-2.5), 141.89(C-3,4), 139.91, 138.87, 130.01, 128.83, 127.92, 127.38, 126.18, 125.52(Ph), IR( $\text{cm}^{-1}$ ),  $\delta_{\text{Si-Me}} = 1240$ .

$\text{R,R}'\text{-TPSCp}(\text{R}=\text{Me}/\text{R}'=\text{Cl})$ (I-b); mp.  $190\text{--}191^\circ\text{C}$ (lit.<sup>20</sup>  $194\text{--}195^\circ\text{C}$ ), Anal. Calcd. (found) for  $\text{C}_{29}\text{H}_{23}\text{ClSi}$ , C, 80.07 (79.83), H, 5.33(5.41), mass *m/e* 434( $\text{M}^+$ ), 419( $\text{M}^+-\text{Me}$ ),  $^1\text{H-NMR}(\text{CDCl}_3, \text{ppm})$ , 0.86(s, 3H, SiMe), 6.7-7.2(brd. m, 2OH, Ph),  $^{13}\text{C-NMR}(\text{CDCl}_3, \text{ppm})$ , 0.34(SiMe), 155.30(C-2.5), 137.98 (C-3,4), 137.83, 136.62, 130.02, 129.35, 128.43, 127.93, 127.15, 126.71(Ph), IR( $\text{cm}^{-1}$ ),  $\delta_{\text{Si-Me}} = 1245$ .

$\text{R,R}'\text{-TPSCp}(\text{R}=\text{Ph}/\text{R}'=\text{Cl})$ (I-c); mp.  $169^\circ\text{C}$ (lit.<sup>20</sup>  $181\text{--}183^\circ\text{C}$ ), Anal. Calcd. (found) for  $\text{C}_{34}\text{H}_{25}\text{ClSi}$ , C, 82.26(81.97), H, 5.04(4.97), mass *m/e* 497( $\text{M}^+$ ), 462( $\text{M}^+-\text{Cl}$ ),  $^1\text{H-NMR}(\text{CDCl}_3, \text{ppm})$ , 6.7-7.2(brd. m, Ph), 7.2-7.8(brd. m, Ph),  $^{13}\text{C-NMR}(\text{CDCl}_3, \text{ppm})$ , 156.30(C-2.5), 137.82(C-3,4), 134.39, 131.16, 130.31, 128.50(SiPh), 137.22, 135.77, 129.71, 129.21, 127.97, 127.70, 126.94, 126.40(Ph).

**Tricarbonyl(1,1-dimethyl-3,4,5-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene)chromium(II-a) and (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-ylidibenzene)bis(tricarbonylchromium) (III)**. A mixture of 1.24g (3.0 mmol) of I-a and 1.54g (7.0 mmol) of chromiumhexacarbonyl in 80 ml of toluene was refluxed with stirring for 60 hrs. The greenish yellow solution of toluene was changed to orange, scarlet and finally dark-red. After the solvent was distilled off in vacuum, with sublimating of the residual chromiumhexacarbonyl followed

by washing with 20 ml of *n*-pentane, 70 ml of *n*-hexane was given to the residue. The extraction of the residue with *n*-hexane was repeated 5-6 times and collected. The *n*-hexane solution of orange was standed for 20 hrs at room temperature, the orange solution with black precipitate was obtained. After seperatin of the precipitate by decantation, the solution was condensed to a  $\sigma$  half and kept at room temperature for 72 hrs, then scarlet crystals were obtained. Recrystallization from *n*-hexane two or three times gave 0.42g of scarlet crystals (II-a). And, after extraction of the residue insoluble to *n*-hexane with 70 ml of ether, the ether solution of red was standed for 20 hrs at room temperature. Then, the ether solution was decantated, crystalization for one week at room temperature gave 0.93g of red crystals (III).

**II-a:** Scarlet crystal (Yield, 25%), mp, 172 °C(decomp.), Anal. Calcd.(found) for  $C_{33}H_{26}O_3SiCr$ , C; 71.97(71.04), H; 4.75(4.61), Mass, 550( $M^+$ ) 522( $M^+-CO$ ), 466( $M^+-3CO$ ), 414(ligand),  $^1H$ -NMR( $CDCl_3$ , ppm), 0.67(s, 6H, Si- $CH_3$ ), 4.87-5.45(brd.m, 5H, Cr-Ph), 6.64-7.23(brd. m, 15H, Ph), IR( $cm^{-1}$ ),  $\nu_{co}$  = 1965, 1905, 1880.

**III:** Red crystal(Yield, 45%), mp, 184 °C (decomp.), Anal. Calcd. (found) for  $C_{33}H_{26}ClO_3SiCr_2$ , C; 62.79(63.01), H; 4.75 (3.92), Mass, 686( $M^+$ ), 550( $M^+-Cr-6CO$ ), 518( $M^+-6CO$ ), 466( $M^+-Cr-6CO$ ), 414(ligand),  $^1H$ -NMR ( $CDCl_3$ , ppm), 0.86 (s, 6H, Si- $CH_3$ ), 4.74-5.44(brd. m, 10H, Cr-Ph), 6.64-7.23(brd.m, 10H, Ph), IR( $cm^{-1}$ ),  $\nu_{co}$  = 1950, 1865.

**Reaction of II-a with Chromiumhexacarbonyl.** A mixture of 0.55g(1 mmol) of II-a and 0.44g(2 mmol) of chromiumhexacarbonyl in 60 ml of toluene was refluxed with stirring for 40 hrs. The scarlet solution was changed to dark-red. The remaining treatment was same above procedure, Yield (40%).

II-b and II-c were prepared with 1.0 mmol of the corresponding  $R,R'$ -TPSCp( $R=Me/R'=Cl$ ,  $R=Ph/R'=Cl$ ) with 3.0 mmol of chromiumhexacarbonyl principally in identical manner as described in the preparation of II-a, III, II-b and II-c were crystalized from ether-pentane, ether, respectively.

**II-b.** Red crystal (Yield, 0.26g, 60%), mp. 162 °C, Anal. Calcd. (found) for  $C_{32}H_{23}ClO_3SiCr$ , C; 67.31(68.27), H; 4.06(4.06), Mass, 570( $M^+$ ), 486( $M^+-3CO$ ), 434(ligand),  $^1H$ -NMR( $CDCl_3$ , ppm), 1.12(s, 3H, Si- $CH_3$ ), 4.81-5.82(brd. m, 5H, Cr-Ph), 6.70-7.23(brd.m, 15H, Ph), IR( $cm^{-1}$ ),  $\nu_{co}$  = 1950, 1880.

**II-c:** Red crystal(0.38g, 60%), mp. 178 °C, Anal. Calcd. (found) for  $C_{37}H_{25}ClO_3SiCr$ , C; 70.19(68.35), H; 3.98(4.08), Mass, 632( $M^+$ ), 604( $M^+CO$ ), 548( $M^+-3CO$ ), 496(ligand),  $^1H$ -NMR( $CDCl_3$ , ppm), 7.23-7.95(brd.m.5H, Ph), 4.82-5.26 (brd. m, 5H, Cr-Ph), 6.82-7.23(brd.m, 15H, Ph), IR( $cm^{-1}$ ),  $\nu_{co}$  = 1960, 1915, 1895, 1875.

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