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SYNTHESIS AND SOME REACTIONS OF DICHLORO(PENTAMETHYLCYCLOPENTADIENYL)RUTHENIUM(III) OLIGOMER

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Paramagnetic ruthenium(III) complex, $[(C_5Me_5)RuCl_2]_n$, is prepared by the reaction of $RuCl_3 \cdot H_2O$ with C_5Me_5H in refluxing ethanol. Treatment of $[Cp^*RuCl_2]_n$ ($Cp^* = C_5Me_5$) with cyclic dienes or α,ω-bis(diphenylphosphino)alkanes gives diamagnetic Ru(II) complexes, Cp*RuCl(diene) or Cp*RuCl(dipos), respectively. Cationic diene complex of ruthenium is formed by the reaction of Cp*RuCl(2,5-norbornadiene) with $AgBF_4$.

The chemistry of transition metal complexes having pentamethylcyclopentadienyl as auxiliary ligand has been the subject of increasing attention. Only a few examples of ruthenium(III) complexes containing cyclopentadienyl or pentamethylcyclopentadienyl ligands are reported while there is a vast chemistry of ruthenocene and cyclopentadienylruthenium(II) complexes.$^{1)}$ Grubbs and Bercaw$^{2)}$ recently reported the preparation of $[(C_5Me_5)RuCl_2]_n$ via a direct reaction of $RuCl_3 \cdot 3H_2O$ with pentamethylcyclopentadiene in refluxing methanol. We synthesized the same complex independently. In the present letter, we describe the synthetic route to dichloro(pentamethylcyclopentadienylruthenium(III), $[(C_5Me_5)RuCl_2]_n$, and a number of new complexes derived therefrom.

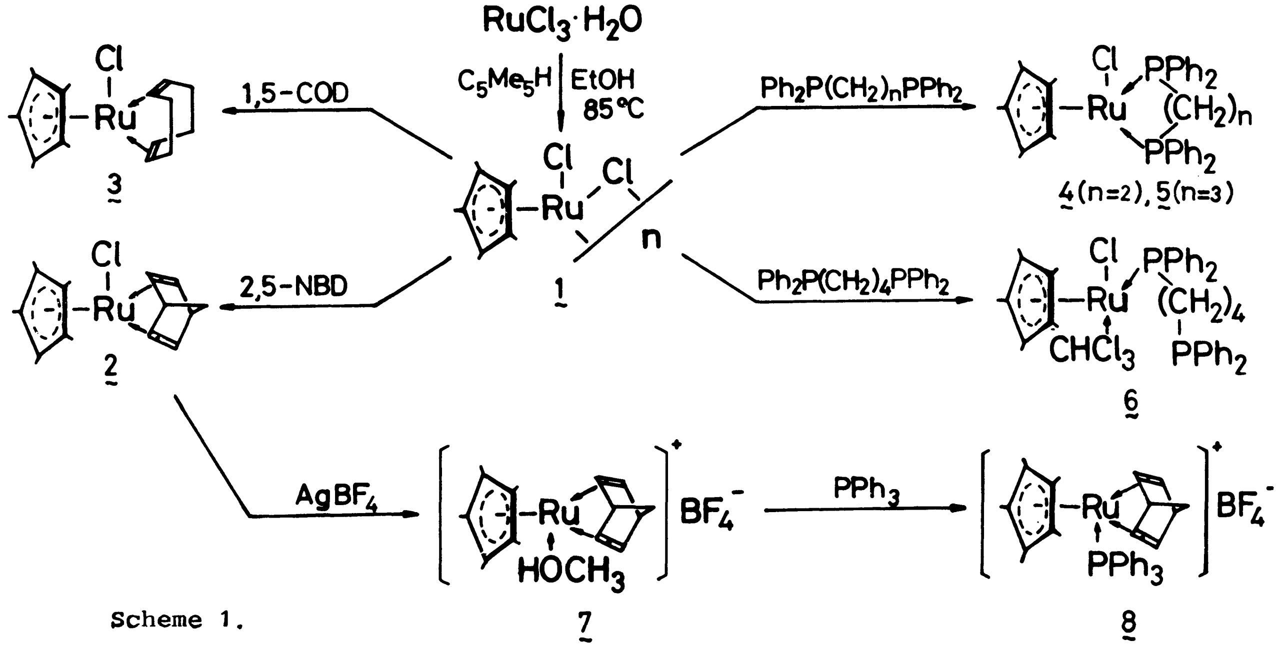
Dichloro(pentamethylcyclopentadienyl)ruthenium(III) (1) was prepared by the reaction of $RuCl_3 \cdot H_2O$ (6.62 mmol) with pentamethylcyclopentadiene (15.1 mmol) in refluxing ethanol (25 ml) for 3 h. (Eq. 1) Dark brown crude product precipitated in the flask was collected on a fine frit and was successively washed with two portions of 5 ml of ethanol and two portions of 5 ml of dry diethyl ether. Drying under reduced pressure gave the complex 1 in 61% yield.

$$RuCl_3 \cdot H_2O + C_5Me_5H \xrightarrow[\text{EtOH}]{85^\circ\text{C, 3h}} \underset{\underline{1}}{[(C_5Me_5)RuCl_2]_n} \qquad (1)$$

Complex 1 was characterized by IR and ^{1}H-NMR spectra as well as by elemental analysis.$^{3)}$ Appearance of a broad signal for methyl protons ($w_{\frac{1}{2}}$ = 17 Hz) at δ4.90 ppm in ^{1}H-NMR spectrum measured in $CDCl_3$ strongly suggested the paramagnetic character of the complex 1. The value of the effective magnetic moment of the complex 1 (μ_{eff} = 1.89 B.M.) was well consistent with d^5 ion of Ru(III). The reaction of $RuCl_3 \cdot H_2O$ with C_5Me_5H in boiling methanol or isopropanol gave a dark brown complex with the same empirical formula, $[(C_5Me_5)RuCl_2]_n$, as 1 in 71-55% yield. The complex formed in methanol or isopropanol was almost insoluble in chloroform or dichloromethane whereas that formed in ethanol was very soluble in such solvents. The former material therefore seemed to be a higher oligomer compared to the latter one.

The complex 1 was easily reduced by the reaction with cyclic dienes or tertiary diphosphines in ethanol to give the corresponding Ru(II) complexes. The results of the reaction of 1 with cyclic dienes or diphosphines are illustrated in Scheme 1. Treatment of 1 with 2,5-norbornadiene or 1,5-cyclooctadiene in ethanol at ambient temperature afforded the stable 18-electron complexes, (C_5Me_5)RuCl(2,5-norbornadiene) (2)[4] or (C_5Me_5)RuCl(1,5-cyclooctadiene) (3),[5] respectively. The ^{1}H-NMR spectrum of the complex 2 measured in $CDCl_3$ at 30 °C (Fig. 1) revealed magnetically equivalent bridge (δ1.30 ppm) protons and two nonequivalent sets of olefinic (δ3.63 and 4.13 ppm) and bridge-head (δ3.68 and 3.79 ppm) protons of coordinated 2,5-norbornadiene. Magnetical nonequivalency of both olefinic and methylene protons of the coordinated 1,5-cyclooctadiene was also observed in the ^{1}H-NMR spectrum of the complex 3. (Fig. 2)

The addition of α,ω-bis(diphenylphosphino)alkane, $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3, and 4), to an ethanol solution of the complex 1 yielded Ru(II) complexes, $(C_5Me_5)RuCl[Ph_2P(CH_2)_2PPh_2]$ (4),[6] $(C_5Me_5)RuCl[Ph_2P(CH_2)_3PPh_2]$ (5),[7] $(C_5Me_5)RuCl[Ph_2P(CH_2)_4PPh_2]$ (6),[8] in 41, 86, and 31% yields, respectively. Characterization of 4, 5, and 6 was made by EI-mass, IR, ^{1}H-, and $^{31}P\{^1H\}$-NMR spectra as well as elemental analysis. $^{31}P\{^1H\}$-NMR spectrum of 5 revealed a broad singlet peak ($w_{\frac{1}{2}}$ = 64 Hz) at δ41.6 ppm whereas a sharp singlet peak was observed at δ50.8 ppm in the $^{31}P\{^1H\}$-NMR spectrum of 4. This would be attributed to the greater



Scheme 1.

steric hindrance between C_5Me_5 and bulky diphosphine ligand in 5 compared to that in 4. The $^{31}P\{^1H\}$-NMR spectrum of the complex 6, which was recrystallized from chloroform, consisted of two sharp singlet peaks at δ46.1 and -11.1 ppm in an equal intensity. This strongly suggests that $Ph_2P(CH_2)_4PPh_2$ is coordinated as a monodentate ligand.

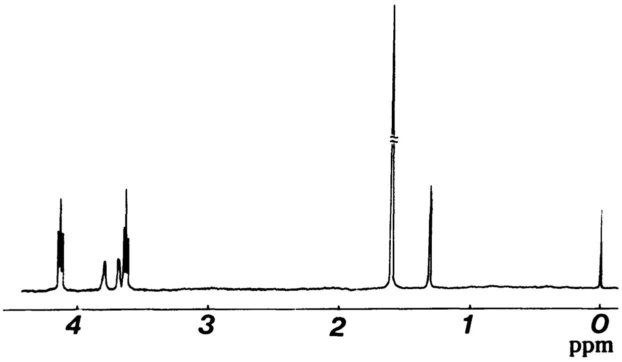


Fig. 1. ^{1}H-NMR (400 MHz) of 2.

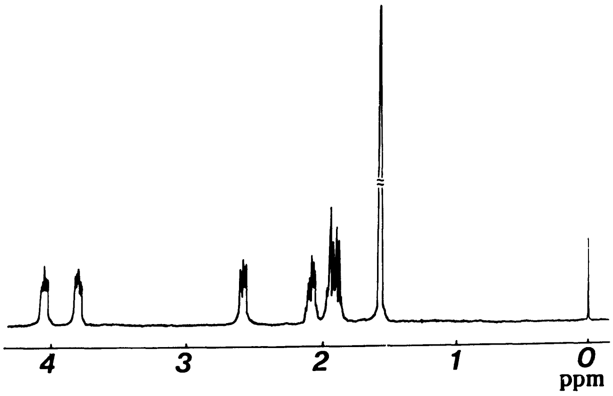


Fig. 2. ^{1}H-NMR (400 MHz) of 3.

A cationic ruthenium(II) complex, 7, was derived from 2. Treatment of 2 with 1 equiv of $AgBF_4$ in ethanol at ambient temperature for 2 h produced a yellowish orange solution of cationic complex together with white precipitates of AgCl. Filtration followed by purification by column chromatography on neutral alumina with methanol gave an orange solid of 7. The ^{13}C-NMR spectrum of 7 revealed five peaks of the coordinated 2,5-norbornadiene together with the signals of C_5Me_5 ligand and weakly coordinated methanol. The peak of the olefinic carbon of the coordinated 2,5-norbornadiene of the complex 7 appeared at somewhat lower field (δ76.3 and 64.2 ppm) than that of the chloro complex 2 (δ71.1 and 55.2 ppm).[9] The difference would reflect the electron-withdrawing ability of the ruthenium center of the cationic complex 7.

The coordinated methanol in 7 was easily substituted by triphenylphosphine. The addition of 1 equiv of triphenylphosphine to a chloroform solution of 7 at ambient temperature gave a cationic ruthenium(II) complex, $[(C_5Me_5)Ru(2,5\text{-norbornadiene})(PPh_3)](BF_4)$ (8), quantitatively. The complex 8 was characterized by IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra as well as elemental analysis.[10]

References

1) M. A. Bennett, M. I. Bruce, and T. W. Matheson, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson; Pergamon Press, Oxford (1982), Vol. 4, pp. 759-795.

2) T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, Organometallics, 3, 274 (1984).

3) 1: Decomp 272 °C. IR (KBr) 2983, 2906, 1478, 1375, 1023, 440 cm^{-1}. ^{1}H-NMR ($CDCl_3$-TMS) δ = 4.90 ($w_{\frac{1}{2}}$ = 17 Hz). μ_{eff} = 1.89 B.M. Found: C, 39.05; H, 5.11; Cl, 24.98%. Calcd for $C_{10}H_{15}Cl_2Ru$: C, 39.10; H, 4.49; Cl, 23.08%.

4) 2: Decomp 175 °C. IR (KBr) 3067, 3010, 2956, 2917, 1452, 1410, 1386, 1379, 1301, 1182, 1075, 1023, 753 cm^{-1}. ^{1}H-NMR (CDCl$_3$-TMS) δ = 1.30 (2H, m), 1.60 (15H, s), 3.63 (2H, m), 3.68 (1H, m), 3.79 (1H, m), 4.13 (2H, m). ^{13}C-NMR (CDCl$_3$-TMS) δ = 9.72 (q, J = 127.5 Hz), 47.01 (d, J = 150.9 Hz), 50.81 (d, J = 151.7 Hz), 55.20 (d, J = 175.8 Hz), 61.42 (t, J = 132.6 Hz), 71.14 (d, J = 180.2 Hz), 94.32 (s). Found: C, 55.34; H, 6.34; Cl, 10.22%. Calcd for $C_{17}H_{23}ClRu$: C, 56.11; H, 6.37; Cl, 9.74%.

5) 3: Mp 128 °C. IR (KBr) 3037, 2959, 2905, 2867, 1470, 1381, 1332, 1158, 1025, 981, 885, 828, 798, 588, 424 cm^{-1}. ^{1}H-NMR (CDCl$_3$-TMS) δ = 1.59 (15H, s), 1.89 (2H, m), 1.94 (2H, m), 2.08 (2H, m), 2.59 (2H, m), 3.81 (2H, m), 4.05 (2H, m). ^{13}C-NMR (CDCl$_3$-TMS) δ = 9.84 (q, J = 127.5 Hz), 28.69 (t, J = 127.5 Hz), 30.89 (t, J = 127.1 Hz), 83.89 (d, J = 154.6 Hz), 84.83 (d, J = 161.2 Hz), 95.48 (s). Found: C, 56.04; H, 7.07; Cl, 9.59%. Calcd for $C_{18}H_{27}ClRu$: C, 56.90; H, 7.16; Cl, 9.33%.

6) 4: Decomp 242 °C. IR (KBr) 3054, 2962, 2900, 1434, 1095, 742, 700, 538 cm^{-1}. ^{1}H-NMR ($C_6D_5CD_3$-TMS) δ = 1.49 (15H, t, J = 1.5 Hz), 1.89 (2H, m), 2.60 (2H, m), 6.99-7.85 (20H, m). ^{31}P-NMR (CDCl$_3$-PPh$_3$) δ = 50.77. EI-MS (intensity) 664 (13.6), 665 (8.7), 666 (12.6), 667 (35.9), 668 (44.7), 669 (66.0), 670 (100), 671 (58.0), 672 (84.5), 673 (37.9), 674 (17.5), 675 (4.9). Found: C, 64.53; H, 5.75%. Calcd for $C_{36}H_{39}ClP_2Ru$: C, 64.52; H, 5.87%.

7) 5: Decomp 253 °C. IR (KBr) 3057, 2974, 2901, 1432, 1098, 748, 697, 515 cm^{-1}. ^{1}H-NMR (CDCl$_3$-TMS) δ = 1.29 (15H, br), 2.32 (3H, m), 3.08 (3H, m), 7.19-7.60 (20H, m). ^{31}P-NMR (CDCl$_3$-PPh$_3$) δ = 41.56 ($w_{\frac{1}{2}}$ = 64 Hz). EI-MS (intensity) 678 (12.6), 679 (7.5), 680 (9.8), 681 (30.5), 682 (37.9), 683 (56.7), 684 (100), 685 (52.4), 686 (72.9), 687 (27.6), 688 (14.2), 689 (7.1). Found: C, 63.05; H, 5.87; Cl, 8.25; P, 7.94%. Calcd for $C_{37}H_{41}ClP_2Ru+0.2CHCl_3$: C, 63.13; H, 5.82; Cl, 8.25; P, 8.76%.

8) 6: Mp 127 °C. IR (KBr) 3047, 2957, 2896, 1434, 1091, 747, 702, 523 cm^{-1}. ^{1}H-NMR ($C_6D_5CD_3$-TMS) δ = 1.28 (15H, t, J = 2.0 Hz), 1.56 (4H, m), 1.92 (4H, m), 6.27 (1H, s), 7.10-7.60 (20H, m). EI-MS (intensity) 692 (11.4), 693 (4.3), 694 (8.6), 695 (33.6), 696 (40.0), 697 (60.7), 698 (100), 699 (48.6), 700 (73.6), 701 (28.6), 702 (16.4), 703 (5.7). Found: C, 56.56; H, 5.30; Cl, 18.02; P, 6.66%. Calcd for $C_{38}H_{43}ClP_2Ru+CHCl_3$: C, 57.28; H, 5.39; Cl, 17.38; P, 7.59%.

9) 7: ^{13}C-NMR (CD_3COCD_3-TMS) δ = 9.27 (q, J = 127.5 Hz), 48.52 (d, J = 150.9 Hz), 49.52 (q, 140.2 Hz, $\underline{C}H_3OH$), 51.97 (d, J = 153.9 Hz), 63.97 (d, J = 134.1 Hz), 64.20 (d, J = 178.8 Hz), 76.31 (d, J = 178.8 Hz), 95.26 (s).

10) 8: Mp 143 °C. IR (KBr) 3026, 2966, 2908, 1483, 1440, 1050, 748, 701, 534 cm^{-1}. ^{1}H-NMR (CDCl$_3$-TMS) δ = 1.10 (2H, m), 1.42 (15H, d, J = 2.0 Hz), 3.88-4.16 (4H, m), 4.28 (2H, m), 7.48-7.72 (15H, m). ^{13}C-NMR (CDCl$_3$-TMS) δ = 10.19, 47.42, 47.57, 48.94, 56.34, 62.58, 64.48, 96.79, 128.42, 128.81, 130.91, 134.93. ^{31}P-NMR (CDCl$_3$-PPh$_3$) δ = 60.53. Found: C, 53.91; H, 4.91; P, 3.99%. Calcd for $C_{35}H_{38}BF_4PRu+CHCl_3$: C, 54.26; H, 4.93; P, 3.89.

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