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Preliminary communication

REACTION OF CATIONIC PALLADIUM(II) AND RHODIUM(I) COMPLEXES WITH THE t-BUTYLPEROXY ANION: PREPARATION OF t-BUTYLPEROXO-PALLADIUM(II) AND -RHODIUM(I) COMPLEXES

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Summary

Treatment of the coordinatively unsaturated cationic complexes, $[(\eta\text{-}C_3H_5)(Ph_3P)_2Pd^{II}]PF_6$ and $[(1,5\text{-}COD)_2Rh^{I}]BF_4$, with potassium t-butylperoxide in dichloromethane gives the t-butylperoxometal complexes; $(\eta\text{-}C_3H_5)(Ph_3P)(t\text{-}BuOO)Pd^{II}$ and $[(1,5\text{-}COD)(t\text{-}BuOO)Rh^{I}](KBF_4)$, via nucleophilic attack by $t\text{-}BuOO^-$ on the cationic metal center.

Recently, transition metal-catalyzed oxidation of olefins to epoxides or ketones with t-butyl hydroperoxide has extensively been studied [1]. The alkylperoxometal complexes (L_nMOOR) are regarded as the key intermediates in these reactions. Therefore great efforts were made for their syntheses and the elucidation of their reactivity. Alkylperoxometal complexes can be obtained from reaction of alkyl hydroperoxides with transition metal complexes [2], from insertion of O_2 into a metal—carbon bond [3], from attack of electrophiles, e.g. RCOX or Ph_3CX, on a peroxoplatinum complex [4], or from reaction of a superoxocobalt complex with a substituted phenol [5]. We describe here the preparation of novel t-butylperoxo-palladium and -rhodium complexes by the reaction of cationic palladium(II), rhodium(I), and rhodium(III) complexes with the t-butylperoxide anion ($t\text{-}BuOO^-$).

Treatment of $[(\eta\text{-}C_5H_5)(1,5\text{-}COD)Pd^{II}]BF_4$ (1) with 1.3 equiv. of t-BuOOLi* in dichloromethane at ambient temperature during 2.5 h gave 8-t-butylperoxy-

*Lithium t-butylperoxide (t-BuOOLi) was prepared by treatment of t-butyl hydroperoxide with lithium hydride in diethyl ether. Potassium t-butylperoxide (t-BuOOK) was prepared similarly using potassium hydride instead of lithium hydride. t-Butyl hydroperoxide was purified prior to use according to the reported method. (D.D. Perrin, W.L.F. Armarego, and D.R. Perrin, Purification of Laboratory Chemicals, 2nd edit., Pergamon Press, Oxford, 1980, p. 149.)

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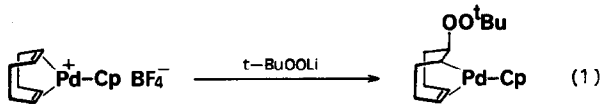
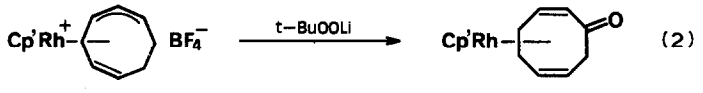
cyclooct-4-en-1-yl(cyclopentadienyl)palladium(II) (2) in 30.4% yield (eq. 1). 2: Orange oil; IR (CH_2Cl_2): 2927 (C—H), 2885 (C—H), 2839 (C—H), 1196 (C—O), 874 cm^{-1} (O—O); ^1H NMR ($CDCl_3$/TMS): δ 1.24 (9H, s, t-Bu), 1.88—2.08 (6H, m), 2.44 (2H, m), 2.64 (1H, m), 4.02 (1H, m), 4.28 (1H, m), 4.72 (1H, m), and 5.70 ppm (5H, s, C_5H_5); ^{13}C NMR ($CDCl_3$/TMS): δ 26.5 ($C(CH_3)_3$), 27.8, 27.9, 28.8, 38.0, 72.4, 79.7 ($C(CH_3)_3$), 84.7, and 87.5 ppm. Found: C, 54.92; H, 6.83. $C_{17}H_{26}O_2Pd$ calcd.: C, 55.37; H, 7.11%. Another example of nucleophilic attack of t-$BuOO^-$ on the coordinated unsaturated



(1)

1 2

hydrocarbon was shown in the reaction of the coordinatively saturated cationic rhodium(III) complex, [(η-C_5Me_5)(1—3:5—6-η-C_8H_{11})Rh^{III}]BF_4 (3), with t-BuOOLi. Treatment of complex 3 with 1.3 equiv. of t-BuOOLi in dichloromethane at ambient temperature gave on work-up (η-C_5Me_5)(cycloocta-2,6-dien-1-one)Rh^I (4) as a yellow crystalline solid in 60.2% yield (eq. 2). 4: M.p. 151°C (dec.); IR (KBr): 2957 (C—H), 2899 (C—H), 2854 (C—H), 2826 (C—H), and 1653 cm^{-1} (C=O); ^1H NMR ($CDCl_3$/TMS): δ 1.54 (1H, m), 1.79 (15H, s), 2.11 (1H, dt, *J* 14.1 and 10.2 Hz), 2.21 (1H, dd, *J* 14.8 and 7.7 Hz), 2.33 (1H, ddt, *J* 6.4, 14.8, and 11.0 Hz), 2.48—2.61 (3H, overlapping), 3.08—3.17 (2H, overlapping), and 3.39 ppm (1H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$/TMS): δ 9.42 (s), 29.9 (s), 34.9 (s), 37.1 (s), 43.8 (d, *J*(Rh—C) 11.7 Hz), 69.8 (d, *J*(Rh—C) 16.1 Hz), 74.5 (d, *J*(Rh—C) 14.7 Hz), 74.8 (d, *J*(Rh—C) 13.2 Hz), 97.6 (d, *J*(Rh—C) 4.4 Hz), and 197.0 (s) ppm. Found: C, 59.67; H, 7.17. $C_{18}H_{25}ORh$ calcd.: C, 60.01; H, 6.99%.



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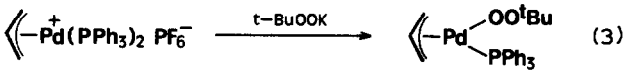
3 4

The ^1H NMR spectrum of 4 was nearly identical with that of the well-characterized (η-C_6H_6)(cycloocta-2,6-diene-1-one)Ru^0 (5), which was obtained from the reaction of [(η-C_6H_6)(1—3:5—6-η-C_8H_{11})Ru^{II}]BF_4 with sodium peroxide or potassium superoxide [6].

The reaction mode of 16-electron cationic complexes with t-$BuOO^-$ is crucially different from that of electronically saturated (18e^-) cationic complexes.

The reaction of η-allylbis(triphenylphosphine)palladium(II) hexafluorophosphate, [(η-C_3H_5)$(Ph_3P)_2Pd^{II}$]PF_6 (6), with potassium t-butylperoxide in toluene at 0°C yielded the t-butylperoxopalladium complex, (η-C_3H_5)(Ph_3P)-(t-BuOO)Pd^{II} (7) (11% yield), which decomposed at room temperature with formation of triphenylphosphine oxide (eq. 3). 7: yellow oil; IR (C_6H_6): 3069 (C—H), 3043 (C—H), 3011 (C—H), 2962 (C—H), 2922 (C—H), 1094 (C—O), and 835 cm^{-1} (O—O); ^1H NMR (C_6D_6-TMS): δ 1.25 (9H, s, $C(CH_3)_3$),

2.98 (2H, d, J 12 Hz), 4.02 (2H, d, J 7 Hz), 5.38 (1H, m), and 7.07—7.73 ppm (15H, m, C_6H_5).

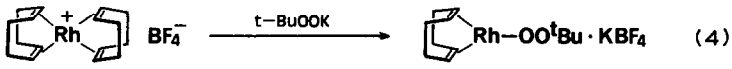


(3)

6 7

The ^{1}H NMR and IR spectra of 7 agree with the structure depicted in eq. 3, and a characteristic band for O—O stretching vibration appeared at 835 cm^{-1} in the IR spectrum of complex 7. The t-butylperoxo ligand in 7 was slowly substituted by a chloride anion if 7 was allowed to stand in a halogenated solvent, e.g. CH_2Cl_2 or $CHCl_3$, to yield (η-C_3H_5)(Ph_3P)$Pd^{II}Cl$ quantitatively.

t-Butylperoxorhodium(I) complex was prepared similarly. Treatment of di-1,5-cyclooctadienerhodium(I) tetrafluoroborate, [(1,5-COD)$_2Rh^I$]BF_4 (8), with 8.0 equiv. t-BuOOK in dichloromethane at ambient temperature for 5 min afforded the 1/1 adduct of (1,5-COD)(t-BuOO)Rh^I and KBF_4 as an orange solid in 56% yield (eq. 4). Microanalytical data, ^{1}H NMR, and IR



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8 9

spectra of the product agree with the proposed structure of 9. 9: M.p. 197—198°C (dec); IR (KBr): 2940 (C—H), 2873 (C—H), 2828 (C—H), 1083 (C—O), 1070 (B—F), 877 cm^{-1} (O—O); ^{1}H NMR ($CDCl_3$/TMS): δ 1.28 (9H, s, C(CH_3)$_3$), 1.37—3.80 ppm (12H, br). Found: C, 34.27; H, 5.30. $C_{12}H_{21}O_2BF_4KRh$ calcd.: C, 33.83; H, 4.97%. Methanolysis of complex 9 gave the well-characterized di-μ-methoxodi-1,5-cyclooctadienedirhodium(I) (10) [7] in quantitative yield via an anion exchange reaction. Incorporation of the t-butylperoxo ligand in complex 9 was confirmed by pyrolysis of 9. Pyrolysis of 9 (0.04 mmol) at 100°C in the presence of 17 equiv. of Ph_3P monitored by ^{31}P NMR resulted in quantitative formation of Ph_3PO (0.08 mmol). In the absence of Ph_3P, pyrolysis of 9 at 220°C in the solid state afforded cyclooctanone and cyclooct-4-en-1-one in 20 and 32% yields, respectively.

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