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REACTION OF PALLADIUM CHLORIDE AND SODIUM TOLYLSULFINATE WITH DIOLEFINS

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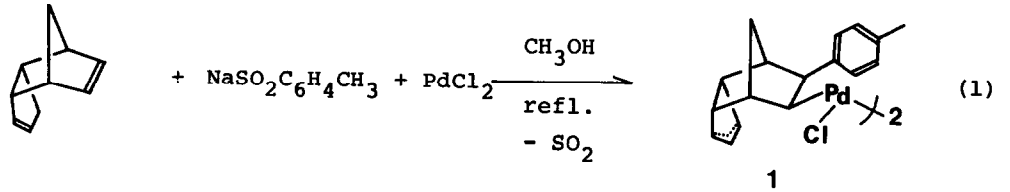
It is well documented that the reaction of palladium salt and arylmercuric chloride generates arylpalladium complex in situ, which reacts with olefins to give the cis-addition products (Heck reaction).[1] By this procedure, Ookita et al.[2] obtained di-μ-chloro-bis-(endo-6-tolyl-3a,4,5,6,7,7a-hexahydro-endo-4,7-methanoindene-endo-5σ,2π)dipalladium(II) 2 and di-μ-chloro-bis-(1-tolylcyclooct-4-ene-8σ,4π)dipalladium(II) 3 from endo-dicyclopentadiene (DCPD) and cycloocta-1,5-diene (COD), respectively (eq 2). Although the reaction of sodium arylsulfinate and palladium salt is another convenient method to generate arylpalladium complex,[3] scant attention has been drawn to this procedure. In connection with arylation of 1,3-dienes,[4] We



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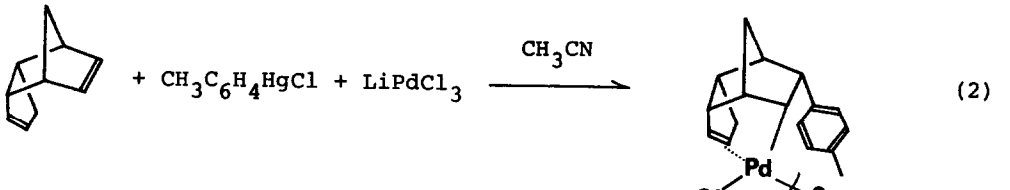

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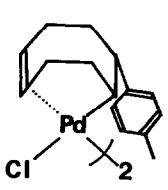

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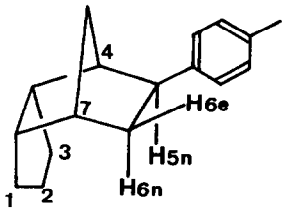

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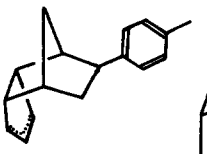

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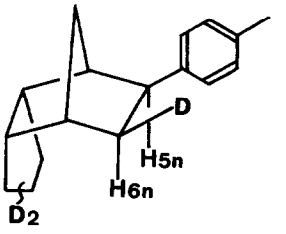

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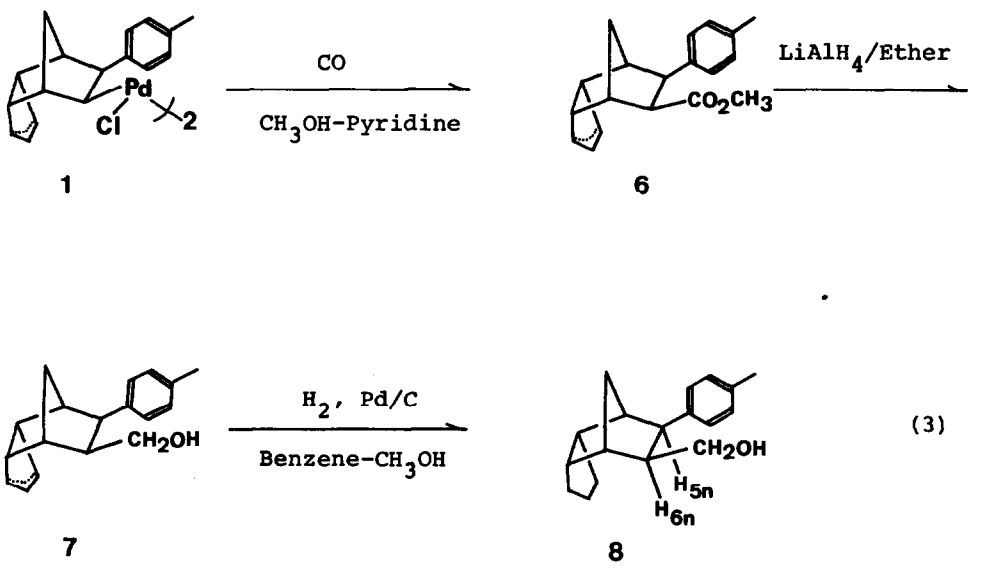
examined the reaction of arylpalladium complex (generated by the latter procedure) with diolefins and found that the arylpalladium generated by these two methods reacted with diolefins in a different manner. While the reaction of palladium chloride and sodium tolylsulsinate with COD provided the expected product 3[5] in 86% yield[6] (methanol reflux for 2-h), the reaction with DCPD gave the different type of compound, di-μ-chloro-bis-(exo-6-tolyl-3a,4,5,6,7,7a-hexahydro-endo-4,7-methanoindene-exo-5σ)dipalladium(II) 1 (eq 1); into a deep red solution of $PdCl_2$ (1.0 mmol) and $NaSO_2Tol$ (2.0 mmol) in 15-ml of methanol was added DCPD (1.5 mmol) and the solution was heated at 60°C for 1-h. Evaporation of methanol and extraction with ethyl acetate (dried over $MgSO_4$) and subsequent purification by column chromatography (silica gel-benzene or neutral alumina-chloroform) provided yellow solid 1[7] (20∿25% yield). The complex 1 is unstable and no satisfactory spectral or analytical data could be obtained; 1 decomposes during NMR measurement[8] in $CDCl_3$ or d_6-benzene depositing palladium black. Hydrogenation of 1 (at atmospheric pressure in acetone, 20-h) gave 4 in quantitative yield: bp 170°C/6 mmHg; NMR ($CDCl_3$, 100 MHz) δ 1.3∿1.8 (m, 9H), 1.95 (d.q, J = 13.0, 9.0, and 2.4 Hz, 1H), 2.15∿2.5 (m, 4H), 2.30 (s, 3H), 2.97 (d.d, J = 9.0 and 5.5 Hz, H_{5n}, 1H), and 7.08 (s, 4H); mass (m/e, rel. int.) 226 (P^+, 55), 143 (16), 134 (39), 129 (23), 121 (45), 119 (38), 118 (100), 106 (73), and 105 (70). ^1H NMR spectrum of 4 shows a very characteristic pair of doublets at δ 2.97 ($J_{5n,6n}$ = 9.0 and $J_{5n,6e}$ = 5.5 Hz) for the H_{5n} proton (the proton on the tolyl-bearing carbon), which becomes a doublet (J = 9.0 Hz) upon saturation at δ 1.50.

The absence of coupling between H_{5n} and bridgehead proton H_4 suggests the exo-configuration of tolyl group,[9] and hence the exo-configuration of palladium, supposing the cis-addition of tolylpalladium.[10] The exo-cis addition of tolylpalladium to the C_5-C_6 double bond would provide 1 as an olefinic isomeric mixture owing to the lack of participation by C_1-C_2 double bond. In fact, a 1:1 mixture of 5[11] was obtained by the selective reduction of Pd-C bond with hydrogen; interestingly, in the presence of 5∿6 eq of pyridine, hydrogenation of 1 proceeded exclusively at the Pd-C bond (under the same conditions to give 4 except for the presence of pyridine), remaining the double bond intact. A mixture of 5 was hydrogenated over Pd/C in ethanol to give a single product 4 quantitatively. No olefin isomerization during reaction was supported by the selective formation of 5-tolylcyclooctene[12] on the hydrogenation of complex 3 in the presence of pyridine; hydrogenation without pyridine gave tolylcyclooctane in 89% yield.

In order to gain further insight into the structure of complex 1, especially around the C_5-C_6 moiety, 1 was converted to 8 by well established procedures (eq 3). Carbonylation of 1 (at 100°C for 8-h in methanol containing 5 eq of pyridine, under 30 atm of CO) provided 6-carbomethoxy derivative 6[13] in 88% yield: bp 165°C/0.15 mmHg (Kugel rohr). Because carbonylation is known



1 6 7 8 (3)

to proceed stereo-specifically with retention of configuration at the carbon bearing palladium,[14] the stereochemistry of carbomethoxy group should reflect the stereochemistry of Pd-C bond. As expected, 6 was obtained as an olefinic isomeric mixture (1:1). Reduction of 6 with $LiAlH_4$ (large excess, in ether at r.t for 2-h) provided 7 (olefinic mixture): bp 140°C/0.035 mmHg, 93% yield. Hydrogenation of 7 was very sluggish and completed by the repeated addition of 5% Pd/C (atmospheric pressure in ethanol-benzene for 2 days) to give rise to homogeneous 8 (vpc and TLC under various conditions) in 93% yield: mp 106.5 ∿107.2°C (from n-hexane); NMR ($CDCl_3$, 100 MHz) δ 0.97 (br. s, OH, 1H), 1.64 (m, 7H), 2.01 (d.t, J = 10.5 and 1.5 Hz, 1H), 2.13 (m, 1H), 2.3∿2.6 (m, 4H), 2.30 (s, 1H), 2.9∿3.3 (m, 3H), and 7.1 (m, 4H); IR (KBr disc) 3300 (s), 1520 (m), 1025 (s), 835 (m), and 760 (m) cm^{-1}; mass (m/e, rel. int.) 256 (P^+, 46), 238 (76), 170 (74), 133 (82), 131 (60), 129 (68), 118 (64), 105 (100), and 91 (84). Remarkable shielding of CH_2-OH protons by tolyl group indicates the cis configuration of these groups. Gradual doping with tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctanedionato(4,6)]europium [$Eu(FOD)_3$] caused remarkable downfield shifts of H_{5n}, H_{6n}, and CH_2OH protons and gave the well separated spectra (11.0 mg of $Eu(FOD)_3$ for 14.6 mg of 8 in 0.5-ml of $CDCl_3$); δ 3.22 (br. q, J = 9.0 Hz, H_{6n}, 1H), 3.53 (d, J = 9.0 Hz, H_{5n}, 1H), 4.40 (m, CH_2O, 2H), and 6.30 (br. s, OH, 1H). Saturation at δ 4.40 changed br. quartet at δ 3.22 to a doublet (J = 9.0 Hz). The H_{5n} proton of 9, which was prepared by the deuteration of 1 with D_2 (atmospheric pressure in methanol containing 4 eq of K_2CO_3)[15] also appeared as a doublet (δ 2.97, J = 9.0 Hz). These observations unequivocally establish that the configuration of both tolyl and hydroxymethyl (and deuterium) groups, accordingly both tolyl and palladium in complex 1, are exo.

Works are under way to isolate 1 in a pure form and to investigate the scope of the selective hydrogenation in the presence of pyridine and selective deuteration[15] of the type of compound 1 or 2 with D_2.[16]

References and Notes

1. P. M. Maitlis, "The Organic Chemistry of Palladium", vol. 1, Academic Press (1971).
2. A. Kasahara, T. Izumi, K. Endo, T. Takeda, and M. Ookita, *Bull. Chem. Soc. Jpn.*, 47, 1967 (1974).
3. (a) B. Chiswell and L. M. Venanzi, *J. Chem. Soc.*, (A), 1246 (1966); (b) K. Garves, *J. Org. Chem.*, 35, 3273 (1970).
4. Y. Tamaru, M. Kagotani, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 368 (1978).
5. Acetylacetonato complex of 3: mp 135°C (from n-hexane); NMR ($CDCl_3$, 100 MHz) δ 1.25 (br.d, J = 13 Hz, 1H), 1.94 (s, 6H), 2.28 (s, 3H), 2.6∿1.9 (m, 8H), 3.34 (m, 1H), 5.27 (s, 1H), 6.13 (q, J = 7 Hz, 1H), 7.04 (d, J = 8 Hz, 2H), and 7.28 (d, J = 8 Hz, 2H); IR (KBr disc) 1580 (s), 1510 (s), 1400 (s) 1260 (m), 1020 (m), and 920 (m).
6. All new products except for 1 gave satisfactory analytical results. Yields refer to the isolated, spectrally and chromatographically homogeneous material; reported yields are not based on recovered starting material.
7. Formation of 1 is independent to the order of addition of reagents.
8. The uncoordinated olefin is suggested by the absorption (δ 5.5∿6.0, multiplet, in $CDCl_3$) in ^1H NMR spectrum of 1.
9. For determination of configuration of norbornane system by NMR spectroscopy, see A. Gaudemer, "Stereochemistry", H. B. Kagan ed., vol. 1, Georg Thieme Publishers Stuttgart (1977).
10. For the exo-cis and endo-cis additions of arylpalladium complexes to norbornene and norbornadienes, see (a) H. Horino, M. Arai, and N. Inoue, *Tetrahedron Lett.*, 647 (1974); (b) A. Segnitz, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 698 (1973).
11. Bp 165°C/3 mmHg; NMR (CCl_4, 100 MHz) δ 1.3∿1.8 (m, 6H), 2.15∿2.8 (m, 4H), 2.26 (s, 3H), 3.1 (m, 1H), 5.65 (m, 2H), and 7.96 (s, 4H); IR (neat film) 3050 (m), 1515 (m), 950 (m), and 690 (m) cm^{-1}; Mass (m/e, rel. int.) 224 (P^+, 32), 222 (20), 157 (37), 156 (100), and 118 (88).
12. Bp 150°C/30 mmHg; NMR (CCl_4, 60 MHz) δ 1.4∿1.95 (m, 6H), 2.0∿2.85 (m, 5H), 2.28 (s, 3H), 5.70 (m, 2H), and 7.00 (s, 4H); IR (neat film) 3020 (m), 1520 (m), 1480 (m), 1120 (w), 1050 (w), 820 (m), 780 (w), and 720 (m); Mass (m/e, rel. int.) 200 (P^+, 28), 185 (22), 172 (94), 157 (37), 145 (34), 143 (37), and 132 (100).
13. Bp 165°C/0.15 mmHg (Kugel rohr); NMR (CCl_4, 100 MHz) δ 1.63 (d, J = 10 Hz, 1H), 2.2∿3.3 (m, 9H), 2.24 (s, 3H), 2.94, 3.00 (two singlets with equal height, OMe, 3H), 5.58 (m, 1H), and 6.93 (s, 4H); IR (neat film) 1740 (s), 1520 (m), 1440 (m), 1360 (m), 1200 (m), 1180 (m), 1130 (m), 1040 (m), and 840 (m) cm^{-1}; Mass (m/e, rel. int.) 282 (P^+, 16), 222 (11), 215 (22), 214 (100), 157 (14), 156 (24), 149 (33), 105 (26), and 91 (21).
14. (a) L. F. Hines and J. K. Stille, *J. Am. Chem. Soc.*, 94, 485 (1972); (b) J. K. Stille and L. F. Hines, *ibid.*, 92, 1798 (1970).
15. Deuteration of 1 in methanol without base or in benzene or acetone proceeded non-stereoselectively. For a similar observation, see J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, 88, 5135 (1966).

16. We are grateful for partial financial support from the Ministry of Education the Japanese Government (Grant-in-Aid for Scientific Research No. 203014).

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