View Article Online / Journal Homepage / Table of Contents for this issue

## Intramolecular, Reversible C–H Oxidative Addition–Reductive Elimination at Rhodium. Reaction of the Intermediate with Different Types of C–H Bonds and Dihydrogen

## Claudio Bianchini, Andrea Meli, Maurizio Peruzzini, and Fabrizio Zanobini

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via J. Nardi, 39, Firenze 50132, Italy

The ortho-metallated complex [{( $Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4$ )}RhH]( $SO_3CF_3$ ) thermally or chemically undergoes reductive elimination of the substituted phenyl group; the N( $CH_2CH_2PPh_2$ )<sub>3</sub>Rh<sup>+</sup> fragment thus formed is stabilized by CO, halides,  $C_2H_4$ , or engaged in oxidative additions of  $H_2$  and C–H bonds from arenes, alkynes, and aldehydes.

Some examples of transition metal complexes capable of inserting into hydrocarbon C–H bonds have recently appeared in the literature.<sup>1</sup> In most instances, these metal systems contain as ancillary ligands pentamethylcyclopentadienyl, carbonyls, and/or trialkylphosphines, but polyphosphane tripod-like ligands are also quite efficient.<sup>2,3</sup> One of these is the potentially tetradentate hybrid ligand  $N(CH_2CH_2PPh_2)_3$ , denoted np<sub>3</sub>.

The fragment  $(np_3)Ir^+$  generated by Cl<sup>-</sup> elimination from  $(np_3)IrCl$  in tetrahydrofuran (THF), undergoes straightforward oxidative addition of a C-H bond from different alkenes, to give *cis*-hydrido( $\sigma$ -alkenyl) derivatives, equation (1).<sup>2</sup> These are quite stable, probably because of the kinetic inertness of iridium complexes.

Since substitution of rhodium for iridium in many reactions gives analogous products but with considerably less stab-



LH = cyclo-octa-1,5-diene (cod), or cyclo-octene (coe)

ility,<sup>1b,4</sup> we have tried to generate the  $(np_3)Rh^+$  moiety through the reductive elimination of CH<sub>4</sub> from the unstable *cis*-(hydride)methyl complex [(np<sub>3</sub>)RhH(Me)]<sup>+</sup>, equation (2). Unexpectedly, under the reaction conditions employed for iridium, the isoelectronic (np<sub>3</sub>)Rh<sup>+</sup> fragment does not insert into the COD or COE unsaturated C-H bonds, but undergoes intramolecular C-H bond oxidative addition of a phenyl group of the np<sub>3</sub> ligand, to give the *ortho*-metallated complex [{(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>PPhC<sub>6</sub>H<sub>4</sub>)}RhH](SO<sub>3</sub>CF<sub>3</sub>) (1), equation (2).<sup>†</sup>

Interestingly, the intramolecular reaction shown in equation (2) can be reversed back to the 16-electron  $(np_3)Rh^+$ species either thermally or by suitable substrates. Electrophilic attack by Me<sup>+</sup> from MeOSO<sub>2</sub>CF<sub>3</sub> on the Rh<sup>1</sup> hydride,  $(np_3)RhH$  (2),<sup>2</sup> in benzene at reflux temperature, gives only the *ortho*-metallated derivative (1). Under the same conditions but at a temperature of 20 °C, a 3 : 1 mixture of (1) and of the hydrido(phenyl) complex [(np<sub>3</sub>)Rh(H)Ph](SO<sub>3</sub>CF<sub>3</sub>) (3) is formed.<sup>‡</sup> Finally, by lowering the temperature to the melting

Selected spectroscopic data: (1) I.r., v(Rh-H) 2000, ortho-metallated phenyl 1560 cm<sup>-1</sup>; <sup>31</sup>P{1H} n.m.r. (positive shifts to high frequency of external 85% H<sub>3</sub>PO<sub>4</sub>) ABCX system (C<sub>6</sub>D<sub>6</sub>, 293 K),  $\delta$  25.70 [P<sub>A</sub>, J(P<sub>A</sub>-P<sub>B</sub>) 22.6, J(P<sub>A</sub>-P<sub>C</sub>) 436.1, J(P<sub>A</sub>-Rh) 104.3 Hz], 12.95, [P<sub>B</sub>, J(P<sub>B</sub>-P<sub>C</sub>) 13.2, J(P<sub>B</sub>-Rh) 80.9 Hz], -34.08 p.p.m. [P<sub>C</sub>, J(P<sub>C</sub>-Rh) 74.8 Hz]; <sup>1</sup>H n.m.r. ([<sup>2</sup>H<sub>8</sub>]THF, 293 K) -11.5 (Rh-H, m, 1H).

(3) I.r., v(Rh-H) 2010, reinforced phenyl vibration 1580 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} n.m.r., AB<sub>2</sub>X system (C<sub>6</sub>D<sub>6</sub>, 293 K),  $\delta$  23.64 [P<sub>A</sub>, J(P<sub>A</sub>-P<sub>B</sub>) 21.9, J(P<sub>A</sub>-Rh) 91.5 Hz],  $\delta$  31.97 p.p.m. [P<sub>B</sub>, J(P<sub>B</sub>-Rh) 115.7 Hz]; <sup>1</sup>H n.m.r. (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  -8.1 (Rh-H, dm, 1H).

(5) I.r.,  $\nu$ (CO) 1975 cm<sup>-1</sup>; <sup>31</sup>P {<sup>1</sup>H} n.m.r., A<sub>3</sub>X system (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  39.55 [*J*(P-Rh) 134.1 Hz]. The solubility of [(np<sub>3</sub>)RhX] (X = Cl, N<sub>3</sub>) is too low to allow any spectroscopic characterization in solution. However the crystals are isomorphous with the trigonal-bipyramidal rhodium derivative (2).<sup>2</sup> The i.r. spectrum of [(np<sub>3</sub>)RhN<sub>3</sub>] shows a strong absorption at 2015 cm<sup>-1</sup> assigned to the stretching mode of the azido ligand.

(7) I.r., v(Rh-H) 2010 cm<sup>-1</sup>, v(C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>) 1430 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} n.m.r., AB<sub>2</sub>X system (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  34.28 [P<sub>A</sub>, J(P<sub>A</sub>-P<sub>B</sub>) 26.3, J(P<sub>A</sub>-Rh) 98.4 Hz],  $\delta$  47.8 p.p.m. [P<sub>B</sub>, J(P<sub>B</sub>-Rh) 123.7 Hz]; <sup>1</sup>H n.m.r. (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  -11.30 (Rh-H, dm, 1H).

(8): I.r., v(Rh-H) 2000,  $v(C\equiv C)$  2120, reinforced phenyl vibration, 1580 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} n.m.r., AB<sub>2</sub>X system (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$ 35.42 [P<sub>A</sub>,  $J(P_A-P_B)$  19.7,  $J(P_A-Rh)$  102.4 Hz],  $\delta$  19.98 p.p.m. [P<sub>B</sub>,  $J(P_B-Rh)$  85.7 Hz]; <sup>1</sup>H n.m.r. (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  -7.70 [Rh-H, dm, 1H,  $J(H-P_{reas})$  170 Hz].

dm, 1H,  $J(H-P_{trans})$  170 Hz]. (9) I.r., v(Rh-H) 1990, v(C=O) 1630 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} n.m.r., AB<sub>2</sub>X system (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  35.32 [P<sub>A</sub>,  $J(P_A-P_B)$  21.6,  $J(P_A-Rh)$ 124.1 Hz],  $\delta$  5.93 p.p.m. [P<sub>B</sub>,  $J(P_B-Rh)$  102.9 Hz]; <sup>1</sup>H n.m.r. (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  -8.2 [Rh-H, ddt, 1H,  $J(H-P_{trans})$  142,  $J(H-P_{cis})$  8, J(H-Rh) 18 Hz].

(10) I.r.,  $v(Rh-H) 2000 \text{ cm}^{-1}$ ;  ${}^{31}P{}^{1}H{}$  n.m.r., AB<sub>2</sub>X system (CD<sub>2</sub>Cl<sub>2</sub>, 223 K),  $\delta$  47.97 [P<sub>A</sub>,  $J(P_A-P_B)$  21.0,  $J(P_A-Rh)$  113.2 Hz],  $\delta$  37.13 p.p.m. [P<sub>B</sub>,  $J(P_B-Rh)$  99.0 Hz]. <sup>1</sup>H n.m.r. ([<sup>2</sup>H<sub>8</sub>]THF, 293 K),  $\delta$  -14.60 (N-Rh-H, m, 1H), -9.0 [P-Rh-H, dm, 1H,  $J(H-P_{trans})$  100 Hz].

(6)  ${}^{31}P{}^{1}H{}$  N.m.r., A<sub>3</sub>X system (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  30.38 p.p.m. [J(P-Rh) 121.8 Hz]. On lowering the temperature to 203 K the pattern changes to give two broad resonances centred at  $\delta$  28.50 and  $\delta$  -5.20 p.p.m.;  ${}^{1}H$  n.m.r. (CD<sub>3</sub>COCD<sub>3</sub>, 293 K),  $\delta$  2.96 (C<sub>2</sub>H<sub>4</sub>, m, 4H).



point of benzene, only the arene activation takes place as evidenced by i.r., <sup>1</sup>H and <sup>31</sup>P n.m.r. spectroscopy. In particular, the <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectrum of (3) consists of an AB<sub>2</sub>X pattern whereas the cyclometallated derivative exhibits an ABCX pattern.

In addition to benzene, other substrates bearing  $sp^2$  and sp C–H bonds, as well as other diatomic and triatomic molecules, are able to shift the equilibrium shown in equation (2) towards

<sup>†</sup> All compounds were isolated as crystalline solids which gave satisfactory elemental analyses.



the  $(np_3)Rh^+$  fragment via addition to (1). Noticeably, the reactions are stoicheiometric and occur at ambient temperature. The  $(np_3)Rh^+$  system can be forced back to the trigonal bipyramidal geometry of the starting product (2) by adding monodentate ligands such as halides or pseudohalides to give (4) and CO to give (5), equation (3). By contrast, reagents such as  $\alpha, \alpha, \alpha$ -trifluorotoluene, phenylacetylene, and acetaldehyde with sp<sup>2</sup> or sp C-H bonds oxidatively add to the rhodium fragment to yield rare, stable examples of octahedral *cis*-(H)( $\sigma$ -organyl)Rh<sup>III</sup> complexes such as [(np<sub>3</sub>)RhH( $\sigma$ -C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)](SO<sub>3</sub>CF<sub>3</sub>) (7), [(np<sub>3</sub>)RhH( $\sigma$ -C<sub>2</sub>Ph)](SO<sub>3</sub>CF<sub>3</sub>) (8), and [(np<sub>3</sub>)RhH( $\sigma$ -COMe)](SO<sub>3</sub>CF<sub>3</sub>) (9), equation (4).†

Complexes with octahedral geometry are also formed by treating (1) in THF with H<sub>2</sub>, Cl<sub>2</sub>, and CS<sub>2</sub>. As a result, *cis*-dihydride (10),<sup>†</sup> *cis*-dichloride (11),<sup>5</sup> and  $\eta^2$ -CS<sub>2</sub> (12)<sup>6</sup> complexes are obtained, equation (5). Reductive elimination

973

of the phenyl group of (1) also occurs when it is treated with  $C_2H_4$  to give the fluxional complex [(np<sub>3</sub>)Rh(C<sub>2</sub>H<sub>4</sub>)](SO<sub>3</sub>CF<sub>3</sub>) (6).† In this case, however, the octahedral solid state geometry changes to trigonal bipyramidal in solution as evidenced by the <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectrum at 293 K which exhibits an A<sub>3</sub>X system.

The  $(np_3)Rh^+$  fragment has potential applications in several catalytic cycles. In this respect, excellent preliminary results have been observed in alkene hydrogenation and hydroformylation reactions and in aldehyde decarbonylations. This is not surprising considering the easy formation of the *cis*-(dihydride),  $\pi$ -ethylene, and *cis*-(hydride)acyl derivatives.

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## References

- See for example: (a) T. T. Wenzel and R. G. Bergman, J. Am. Chem. Soc., 1986, 108, 4856; J. M. Buchanan, J. M. Stryker, and R. G. Bergman, *ibid.*, 1986, 108, 1537; H. Janowicz and R. G. Bergman, *ibid.*, 1983, 105, 3929; R. H. Crabtree and C. P. Parnell, Organometallics, 1984, 3, 1727; J. K. Hoyano and W. A. G. Graham, J. Am. Chem. Soc., 1982, 104, 3723; J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *ibid.*, 1983, 105, 7190; C. J. Cameron, H. Felkin, T. Fillebeen-Khan, N. J. Forrow, and E. Guittet, J. Chem. Soc., Chem. Commun., 1986, 801; (b) W. D. Jones and F. J. Feher, J. Am. Chem. Soc., 1984, 106, 1650.
- 2 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, M. Sabat, and F. Zanobini, Organometallics, 1986, 5, 2557.
- 3 M. Antberg and L. Dahlenburg, Angew. Chem., Int. Ed. Engl., 1986, 25, 260; J. Organomet. Chem., 1986, 312, C67.
- 4 W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562; R. A. Perlana and R. G. Bergman, *ibid.*, 1984, **3**, 508.
- 5 M. Di Vaira, M. Peruzzini, F. Zanobini, and P. Stoppioni, *Inorg. Chim. Acta*, 1983, **69**, 37.
- 6 C. Bianchini, D. Masi, C. Mealli, A. Meli, and M. Sabat, Organometallics, 1985, 4, 1014.