Rhodium(I)–(*N*-heterocyclic carbene)–diphosphine complexes

Hongsui Sun, Xiao-Yan Yu, Paolo Marcazzan, Brian O. Patrick, and Brian R. James

Abstract: Reactions of $[RhCl(COE)(IPr)]_2$ (**1**) and $[RhCl(COE)(IMes)]_2$ (**2**) (COE = cyclooctene; IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) with the diphosphines $Ph_2P(CH_2)_nPPh_2$ and 1,2-bis(diphenylphosphino)benzene (dppbz) give the *N*-heterocyclic carbene (NHC)–diphosphine–rhodium(I) complexes: $RhCl(NHC)[Ph_2P(CH_2)_nPPh_2]$ [NHC = IPr, *n* = 1 (**3**); NHC = IMes, *n* = 1 (**4**); NHC = IPr, *n* = 2 (**5**); NHC = IMes, *n* = 2 (**6**); NHC = IPr, *n* = 4 (**7**); NHC = IMes, *n* = 4 (**8**)] and RhCl(NHC)(dppbz) [NHC = IPr (**9**); NHC = IMes (**10**)]. All the complexes are characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, elemental analysis, and mass spectrometry. Complexes **3**, **7**, and **9** are also characterized crystallographically. In benzene solution, the complexes decompose in the presence of O_2 with formation of the diphosphine dioxide, whereas reaction with CO leads to replacement of the NHC ligand to give known carbonyl–diphosphine complexes.

Key words: rhodium, *N*-heterocyclic carbenes, bis(diphenylphosphino) ligands, crystallography.

Résumé : Les réactions du $[RhCl(COE)(IPr)]_2$ (**1**) et du $[RhCl(COE)(IMes)]_2$ (2) [COE = cyclooctène; IPr = *N*,*N*′-bis(2,6-diisopropylphényl)imidazoline-2-ylidène; IMes = *N*,*N*′-bis(2,4,6-triméthylphényl)imidazoline-2-ylidène] avec les diphosphines $Ph_2P(CH_2)_nPPh_2$ et 1,2-bis(diphénylphosphino)benzène (dppbz) conduisent à la formation de complexes carbène *N*-hétérocyclique (NHC)–diphosphine–rhodium(I): $RhCl(NHC)[Ph_2P(CH_2)_nPPh_2]$ [NHC = IPr, *n* = 1 (**3**); NHC = IMes, *n* = 1 (**4**); NHC = IPr, *n* = 2 (**5**); NHC = IMes, *n* = 2 (**6**); NHC = IPr, *n* = 4 (**7**); NHC = IMes, *n* = 4 (**8**)] et RhCl(NHC)(dppbz) [NHC = IPr (**9**); NHC = IMes (**10**)]. Tous les complexes ont été caractérisés par des analyses élémentaires, par spectroscopie RMN du ^1H, du $^{31}P\{^1H\}$ et du $^{13}C\{^1H\}$ et par spectrométrie de masse. Les complexes **3**, **7** et **9** ont aussi été caractérisés par diffraction des rayons X. En solution dans le benzène, les complexes se décomposent en présence de O_2 avec formation d'oxyde de diphosphine, alors qu'une réaction avec le CO conduit au remplacement du ligand NHC pour conduire aux complexes carbonyl–diphosphines connus.

Mots-clés : rhodium, carbènes *N*-hétérocycliques, ligands bis(diphénylphosphino), cristallographie.

[Traduit par la Rédaction]

Introduction

A just-published special issue of *European Journal of Inorganic Chemistry* demonstrates the growing interest in transition-metal *N*-heterocyclic carbene (NHC) complexes.[1] Seven of the papers in the issue are concerned with Rh–NHC chemistry, including one from our group, which describes reactions of $[RhCl(COE)(NHC)]_2$ complexes with H_2 and with CO, where COE is cyclooctene and NHC is either *N*,*N*′-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr) or *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes).[2] More generally, studies on Rh–NHC systems often pertain to comparisons with the chemistry and catalytic activity of Rh–tertiary phosphine systems, i.e., with replacement of PR_3 ligand(s) by NHC ligand(s) or use of mixed NHC–tertiary phosphine species.[2–5] Of prime interest to our group is the interaction of O_2 with Rh(I) complexes containing coordinated NHC ligands with or without ancillary phosphine ligands. We have shown that RhCl(NHC)(P–N) and *cis*-$RhCl(NHC)(PPh_3)_2$ complexes oxidatively add O_2 to generate "standard" six-coordinate Rh(III)–peroxide species (see Scheme 1), where P–N = *P*,*N*-chelated *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline and NHC = IPr or IMes;[5] in an as yet unpublished work, our X-ray data for a five-coordinate $RhCl(IPr)_2(O_2)$ are also consistent with a peroxide.[6] However, recent communications by Crudden and coworkers[3,4a] report that $RhCl(NHC)_2(O_2)$ (NHC = IPr or IMes) and $RhCl(IMes)(PPh_3)(O_2)$ are best described as being Rh(I) singlet oxygen species. In efforts to understand the nature of this important discrepancy, we decided to synthesize Rh(I)–diphosphine–NHC complexes in the hope that their reactivity toward O_2 might prove helpful — a hope that was not fulfilled!

Received 5 May 2009. Accepted 7 July 2009. Published on the NRC Research Press Web site at canjchem.nrc.ca on 21 August 2009.

This tardy article is dedicated to Professor R.J. Puddephatt on the occasion of his 66th birthday (should have been submitted last year for his 65th!), and in recognition of his contributions to the development of Canadian organometallic chemistry. This article is a belated contribution to a Special Issue dedicated to Professor R.J. Puddephatt (Canadian Journal of Chemistry, January 2009).

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Experimental section

General procedures

All manipulations were performed under an atmosphere of dry Ar using standard Schlenk techniques or in a glove box. Solvents (Fisher Scientific) were dried using standard procedures and, before use, were purged with a stream of Ar. C_6D_6 (Cambridge Isotope Laboratory) was distilled from Na and stored under Ar. The diphosphines were used as received from Strem Chemicals. Complexes $[RhCl(COE)(IPr)]_2$ (**1**) and $[RhCl(COE)(IMes)]_2$ (**2**) were prepared by our literature procedure.[5] NMR spectra were recorded in C_6D_6 at room temperature (~20 °C) either on a Bruker AV 400 or AV 300 spectrometer, data being reported in ppm relative to TMS with the solvent signals as internal references (^{1}H, δ 7.16; ^{13}C, δ 128.38); ^{31}P{H} NMR shifts are relative to external 85% H_3PO_4. *J* values are given in Hz (s = singlet, d = doublet, *t* = triplet, spt = septet, m = multiplet, br = broad, ps = pseudo); assignments were sometimes aided by the use of ^{13}C{^{1}H}-APT and ^{1}H–^{13}C{^{1}H}–HSQC experiments. Mass spectra were obtained on a Kratos MS-50 spectrometer operating in the EI mode or on a Bruker Biflex IV spectrometer operating with a MALDI ion source. Elemental analyses were done on a Carlo Erba EA 1108 elemental analyzer.

RhCl(IPr)($Ph_2PCH_2PPh_2$) (3)

63.8 mg (0.05 mmol) of **1** and 38.5 mg (0.10 mmol) of dppm were dissolved in C_6H_6 (6 mL). The resulting yellow solution became orange on being stirred at room temperature for 5 h and was then concentrated to ~2 mL; hexane (~2 mL) was then added to precipitate the product, which was filtered off and dried in vacuo. Yield: 85 mg (93%). ^{1}H NMR δ: 0.53 (6H, d, J = 6.7, Me), 1.00 (6H, d, J = 6.7, Me), 1.16 (6H, d, J = 6.7, Me), 1.89 (d, 6H, J = 6.7, Me), 3.35 (br t, 2H, J_{HP_A} = 9.0, J_{HP_B} = 8.7, PCH_2P), 3.62 (spt, 2H, J = 6.7, CHMe$_2$), 3.74 (spt, 2H, J = 6.7, CHMe$_2$), 6.79 (s, 2H, NCH), 6.88 (ps t, 6H, *m*-Ph (4H) + *m*-IPr (2H)?), 6.96–6.99 (m, 8H, *o*-Ph (4H) + *p*-Ph (4H)?), 7.23 (t, 2H, $^3J_{HH}$ = 7.6, *p*-IPr), 7.30–7.37 (ps t, 6H, *m*-Ph (4H) + *m*-IPr (2H)?), 7.88–7.95 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 22.87, 24.36, 26.87, 27.03, 29.09, 29.69, 48.29 (dd, J_{CP} = 19, J_{CP} = 30, PCH_2P), 123.78, 124.52, 124.91, 128.05, 128.21, 128.31, 128.88, 129.48, 129.77, 133.01 (d, J_{CP} = 22, C_{Ph}P), 133.96 (d, J_{CP} = 12, C_{Ph}P), 136.35, 136.65, 136.73, 137.02, 138.13, 144.89, 149.16, 195.45 (ddd, J_{CP_A} = 10, J_{CP_B} = 48, J_{CRh} = 128, Rh–*C*). ^{31}P{H} NMR: AB portion of the P_A, P_B, Rh (ABX) spin system simulated by the parameters: δ_A = –35.68, δ_B = –20.92, J_{AB} = 101.0, J_{AX} = 104.0, J_{BX} = 178.0 (see text). MS (EI) (*m*/*z*): 910 [M]$^+$, 387 [IPr – 1]$^+$. Anal calcd. for $C_{52}H_{58}N_2ClP_2Rh$: C 68.55, H 6.42, N 3.08; found: C 68.8, H 6.4, N 2.9. X-ray quality crystals of **3** containing 0.5 mol C_6H_6 solvate were grown by layering a C_6H_6 solution of the compound with hexane.

RhCl(IMes)($Ph_2PCH_2PPh_2$) (4)

The synthetic procedure for complexes **4**–**10** follows that given for **3**; here, 55.0 mg (0.05 mmol) of **2**, 38.6 mg (0.10 mmol) of dppm, and C_6H_6 (5 mL) were used. Yield: 74 mg (89%). ^{1}H NMR δ: 1.73 (s, 6H, *o*-Me), 2.22 (s, 6H, *o*-Me), 2.77 (s, 6H, *p*-Me), 3.40 (br t, 2H, J_{HP_A} = 9.1, J_{HP_B} = 8.8, PCH_2P), 6.25 (s, 2H, NCH), 6.60 (s, 2H, *m*-IMes), 6.88 (s, 2H, *m*-IMes), 6.95–7.09 (m, 12H, *o*-Ph (4H) + *m*-Ph (4H) + *p*-Ph (4H)?), 7.43–7.49 (m, 4H, *m*-Ph), 7.80–7.87 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 19.45 (Me), 21.02 (Me), 21.61 (Me), 51.11 (dd, J_{CP} = 18, J_{CP} = 23, PCH_2P), 122.93 (NCH), 122.97 (NCH), 128.99, 129.40, 130.31, 131.70, 131.92, 133.84 (d, J_{CP} = 20, C_{Ph}P), 133.96 (d, J_{CP} = 16, C_{Ph}P), 135.35, 136.69, 136.98, 137.79, 138.07, 138.33, 138.54, 193.15 (ddd, J_{CP_A} = 10, J_{CP_B} = 47, J_{CRh} = 129, Rh–*C*). ^{31}P{H} NMR: AB portion of the P_A, P_B, Rh (ABX) spin system simulated by the parameters δ_A = –33.57, δ_B = –19.93, J_{AB} = 107.0, J_{AX} = 102.0, J_{BX} = 179.0 (see text). MS (EI) (*m*/*z*): 826 [M]$^+$, 790 [M – HCl]$^+$, 303 [IMes – 1]$^+$. Anal. calcd. for $C_{46}H_{46}N_2ClP_2Rh$: C 66.81, H 5.61, N 3.39; found: C 66.8, H 5.6, N 3.3.

RhCl(IPr)($Ph_2PCH_2CH_2PPh_2$) (5)

Complex **5** was prepared using 50.0 mg (0.04 mmol) of **1**, 31.0 mg (0.08 mmol) of dppe, and 10 mL C_6H_6. Yield: 66 mg (91%). ^{1}H NMR δ: 0.40 (d, 6H, J = 6.8, Me), 0.90 (d, 6H, J = 6.8, Me), 1.11 (d, 6H, J = 6.8, Me), 1.42–1.64 (m, 4H, CH_2-dppe), 1.68 (d, 6H, J = 6.8, Me), 3.38 (m, 2H, CHMe$_2$), 3.81 (m, 2H, CHMe$_2$), 6.81 (s, 2H, NCH), 6.87 (d, 2H, J = 7.4, *m*-IPr), 6.93 (t, 4H, J = 7.0, *m*-Ph), 7.02 (t, 2H, J = 7.0, *p*-Ph), 7.07–7.14 (m, 6H, *o*-Ph (4H) + *p*-Ph (2H)?), 7.26 (t, 2H, J = 7.7, *p*-IPr), 7.35 (d, 2H, J = 7.6, *m*-IPr), 7.45 (t, 4H, J = 8.5, *m-Ph*), 7.73–7.78 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 22.90, 24.34, 27.04, 27.17, 28.90, 29.71, 32.84 (d, J_{CP} = 25, *C*H$_2$), 33.17 (d, J_{CP} = 23, *C*H$_2$), 123.90, 124.86, 124.94, 127.83, 127.92, 127.98, 128.93, 129.16, 129.75, 133.64 (d, J_{CP} = 12, C_{Ph}P), 135.16 (d, J_{CP} = 12, C_{Ph}P), 136.20, 136.60, 137.94, 138.25, 144.91, 149.61, 196.72 (dd, J_{CP} ~ 48, J_{CRh} = 121). ^{31}P{H} NMR δ: 62.10 (dd, $^2J_{PP}$ = 38, $^1J_{RhP}$ = 123), 65.84 ($^2J_{PP}$ = 38, $^1J_{RhP}$ = 208). MS (EI) (*m*/*z*): 924 [M]$^+$, 536 [M – IPr]$^+$, 387 [IPr – 1]$^+$. Anal. calcd. for $C_{53}H_{60}N_2ClP_2Rh$: C 68.81, H 6.54, N 3.03; found: C 68.5, H 6.4, N 3.0.

RhCl(IMes)($Ph_2PCH_2CH_2PPh_2$) (6)

Complex **6** was prepared using 75.0 mg (0.07 mmol) of **2**, 54.0 mg (0.14 mmol) of dppe, and 10 mL C_6H_6. Yield: 98 mg (86%). ^{1}H NMR δ: 1.23–1.24 (m, 4H, CH_2-dppe), 1.61 (s, 6H, *o*-Me), 2.23 (s, 6H, *o*-Me), 2.79 (s, 6H, *p*-Me), 6.23 (s, 2H, NCH), 6.60 (s, 2H, *m*-IMes), 6.85 (s, 2H, *m*-IMes), 6.97–7.11 and 7.04–7.08 (m, 12H, *o*-Ph (4H) + *m*-Ph(4H) + *p*-Ph (4H)?), 7.51 (t, 4H, J = 8, *m*-Ph), 7.80 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 19.72 (Me), 21.56 (Me), 21.59 (Me), 32.05 (d, J_{CP} = 25, *C*H$_2$), 32.40 (d, J_{CP} = 25, *C*H$_2$), 123.16 (NCH), 127.77, 127.86, 127.93, 128.87, 128.93, 129.01, 129.14, 130.39, 134.52 (d, J_{CP} = 11, C_{Ph}P), 135.04 (d, J_{CP} = 10, C_{Ph}P), 135.58, 137.57, 138.49, 138.53, 139.04, 139.36. AB portion of the P_A, P_B, Rh (ABX) spin system simulated by the parameters δ_A = –64.26, δ_B = –64.96, J_{AB} = 36.6, J_{AX} = 125.7, J_{BX} = 205.7 (see text). MS (EI) (*m*/*z*): 840 [M]$^+$, 804 [M – HCl]$^+$, 536 [M – IMes]$^+$, 303 [IMes – 1]$^+$. Anal. calcd. for $C_{47}H_{48}N_2ClP_2Rh$: C 67.13, H 5.76, N 3.33; found: C 67.0, H 5.8, N 3.23.

RhCl(IPr)[$Ph_2P(CH_2)_4PPh_2$] (7)

Complex **7** was prepared by using 63.8 mg (0.05 mmol) of **1**, 42.7 mg (0.10 mmol) of dppb, and 10 mL C_6H_6. Yield: 76 mg (80%). ^{1}H NMR δ: 0.59 (br s, 6H, Me), 1.05 (m,

12H, Me), 1.29 (br s, 6H, Me), 1.72 (br s, 4H, CH_2), 1.85 (br s, 4H, CH_2), 3.56 (br s, 4H, CHMe$_2$), 6.89 (s, 2H, NCH), 6.98–7.08 (m, 16H, *Ar*), 7.30–7.41 (m, 10H, *Ar*). ^{13}C{H} NMR δ: 21.86 (Me), 23.89 (*C*H$_2$), 23.97, 25.14, 25.58 (d, J_{CP} = 20, P*C*H$_2$), 27.34 (Me), 29.64 (Me), 29.73 (Me), 30.24 (*C*H$_2$), 36.17 (d, J_{CP} = 25, P*C*H$_2$), 123.61, 124.05, 125.20, 127.15 (d, J_{CP} = 9, C_{Ph}P), 128.30, 128.69, 128.93, 129.03, 129.61, 131.42, 131.51, 131.58, 133.36 (d, J_{CP} = 11, C_{Ph}P), 145.10, 150.55. ^{31}P{H} NMR δ: 13.85 ($^2J_{PP}$ = 48, $^1J_{RhP}$ = 114), 48.94 (dd, $^2J_{PP}$ = 48, $^1J_{RhP}$ = 208). MS (MALDI) (*m*/*z*): 952 [M]$^+$. Anal. calcd. for $C_{55}H_{64}ClN_2P_2Rh$: C 69.30, H 6.77, N 2.94; found: C 69.5, H 6.7, N 3.1. X-ray quality crystals of **7** were grown by layering a C_6H_6 solution of the compound with hexane.

RhCl(IMes)[Ph$_2$P(CH$_2$)$_4$PPh$_2$] (8)

The yellow complex **8** was obtained using 75.0 mg (0.07 mmol) of **2**, 58.0 mg (0.14 mmol) of dppb, and 10 mL of benzene. Yield: 91 mg (77%). ^{1}H NMR δ: 1.91 (s, 6H, *o*-Me), 2.09 (m, 4H, CH_2), 2.26 (s, 6H, *o*-Me), 2.46 (br s, 4H, CH_2), 2.83 (s, 6H, *p*-Me), 6.29 (s, 2H, NCH), 6.75 (s, 2H, *m*-IMes), 6.90–7.11 (m, 14H, *o*-Ph (4H) + *m*-Ph (4H) + *p*-Ph (4H) + *m*-IMes (2H)?), 7.32 (t, 4H, *J* = 8, *m*-Ph), 7.62 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 19.90 (Me), 21.89 (Me), 22.48 (Me) 24.08 (*C*H$_2$), 32.74 (d, *J* = 18, P–*C*H$_2$), 32.99 (*C*H$_2$), 122.03, 122.05, 123.11, 126.84 (d, J_{CP} = 10, C_{Ph}P), 127.64, 127.82, 129.13, 129.54 (d, J_{CP} = 8, C_{Ph}P), 133.44, 134.39, 134.65, 134.92, 135.43, 135.68, 137.38, 137.41, 138.20, 138.60, 138.90, 144.34. ^{31}P{H} NMR δ: 12.38 (dd, $^2J_{PP}$ = 48, $^1J_{RhP}$ = 118), 54.04 ($^2J_{PP}$ = 48, $^1J_{RhP}$ = 207). MS (MALDI) (*m*/*z*): 868 [M]$^+$. Anal. calcd. for $C_{49}H_{52}ClN_2P_2Rh$: C 67.70, H 6.04, N 3.23; found: C 67.9, H 6.0, N 3.3.

RhCl(IPr)(Ph$_2$PC$_6$H$_4$PPh$_2$) (9)

The orange complex **9** was obtained using 55.0 mg (0.04 mmol) of **1** and 44.0 mg (0.10 mmol) of dppbz in 5 mL of C_6H_6. Crystalline material contained 0.5 mol solvate C_6H_6. Yield: 82 mg, 96%. Dried material was of the formulation $C_{57}H_{60}ClN_2P_2Rh$. ^{1}H NMR δ: 0.70 (d, 6H, *J* = 6.7, Me), 0.90 (d, 6H, *J* = 6.7, Me), 1.10 (d, 6H, *J* = 6.7, Me), 1.65 (d, 6H, *J* = 6.5, Me), 3.37 (m, 2H, CHMe$_2$), 3.91 (m, 2H, CHMe$_2$), 6.72 (br s, 2H, NCH), 6.80–6.82 (m, 4H, *m*-Ph), 6.89–6.95 (br t, 6H, *J* ~ 6.5), 7.09–7.15 (m, 8H), 7.25 (d, 2H, *J* = 7.6), 7.43 (ps t, 6H), 7.81 (m, 4H). ^{13}C{H} NMR δ: 22.73, 24.27, 26.99, 27.14, 29.21, 29.62, 123.63, 124.99, 127.87, 127.97, 128.32, 128.51, 128.69, 128.92, 129.10, 129.81, 133.10, 133.22, 135.13 (d, J_{CP} = 11, $C_{C_6H_4}$P?), 137.10 (d, J_{CP} = 45, C_{Ph}P?), 138.55, 139.57 (d, J_{CP} = 36, C_{Ph}P?), 144.47, 149.05, 194.96 (ddd, J_{CP_A} = 11, J_{CP_B} = 48, J_{CRh} = 122, Rh–*C*). ^{31}P{H} NMR δ: 65.96 (dd, $^2J_{PP}$ = 39, $^1J_{RhP}$ = 205), 71.36 ($^2J_{PP}$ = 39, $^1J_{RhP}$ = 124). MS (EI) (*m*/*z*): 972 [M]$^+$, 387 [IPr – 1]$^+$. Anal. calcd: C 70.35, H 6.22, N 2.88; found: C 70.6, H 6.3, N 2.7. The layering method given for complex **3** yielded X-ray quality crystals of **9** again containing 0.5 mol C_6H_6 solvate.

RhCl(IMes)(Ph$_2$PC$_6$H$_4$PPh$_2$) (10)

The orange complex **10** was obtained using 55.0 mg (0.05 mmol) of **2** and 44.0 mg (0.10 mmol) of dppbz in 5 mL of C_6H_6. Yield: 71 mg (80%). ^{1}H NMR δ: 1.62 (s, 6H, *o*-Me), 2.16 (s, 6H, *o*-Me), 2.74 (s, 6H, *p*-Me), 6.21 (s, 2H, NCH), 6.53 (s, 2H, *m*-IMes), 6.66–6.71 (m, 2H, *o*-C_6H_4), 6.74 (s, 2H, *m*-IMes), 6.95–7.04 (m, 12H, *o*-Ph (4H) + *m*-Ph (4H) + *p*-Ph (4H)), 7.25 (ps t, 2H, *m*-C_6H_4), 7.67 (t, 4H, *J* = 8.6, *m*-Ph), 7.79 (m, 4H, *o*-Ph). ^{13}C{H} NMR δ: 18.58, 20.79, 122.48, 127.09, 127.18, 127.25, 127.34, 127.81, 127.96, 128.16, 128.37, 128.88 (d, J_{CP} = 3, C_{Ph}P?), 129.21 (d, J_{CP} = 4, C_{Ph}P?), 129.65, 130.57, 130.70, 131.68, 131.83, 133.99, 134.11, 134.22, 134.32, 134.68, 136.38, 136.80, 137.53, 137.64, 138.02, 138.36, 192.32 (dd, J_{CP} ~ 9, J_{CRh} = 118, Rh–*C*). ^{31}P{H} NMR: AB portion of the P_A, P_B, Rh (ABX) spin system simulated by the parameters δ_A = –66.77, δ_B = –67.33, J_{AB} = 39.60, J_{AX} = 206.8, J_{BX} = 125.6 (see text). MS (EI) (*m*/*z*): 888 [M]$^+$, 303 [IMes – 1]$^+$. Anal. calcd. for $C_{51}H_{48}ClN_2P_2Rh$: C 68.90, H 5.45, N 3.15; found: C 69.0, H 5.3, N 3.3.

X-ray crystallographic analysis of complexes 3, 7, and 9

Measurements were made at 173.0(1) K on a Bruker X8 APEX diffractometer with graphite-monochromated Mo-Kα radiation (0.71 069 Å). Data were collected and integrated using the Bruker SAINT software package[7] and were corrected for absorption effects using the multi-scan SADABS technique.[8] All structures were solved by direct methods,[9] and refinements were performed using the SHELXTL program.[10] All non-hydrogen atoms were refined anisotropically and all H atoms were included in calculated positions but not refined.

Crystal data for 3

$C_{52}H_{58}N_2ClP_2Rh{\cdot}0.5C_6H_6$, fw = 949.31, orange tablet, size 0.15 mm × 0.20 mm × 0.50 mm, monoclinic, space group *P* 2$_1$/*n* (No. 14), *a* = 11.0616(2) Å, *b* = 21.9905(4) Å, *c* = 20.1095(4) Å, β = 90.774(1)°, *V* = 4891.2(2) Å^3, *Z* = 4, D_{calcd} = 1.291 g cm^{-3}, μ = 0.507 mm^{-1}. *F*(000) = 1988.00, 62 508 total reflections (11 674 independent of symmetry, 8726 for $I > 2\sigma(I)$), 558 variables, residuals (refined on F^2, all data): *R*1 = 0.038, *wR*2 = 0.088.

Crystal data for 7

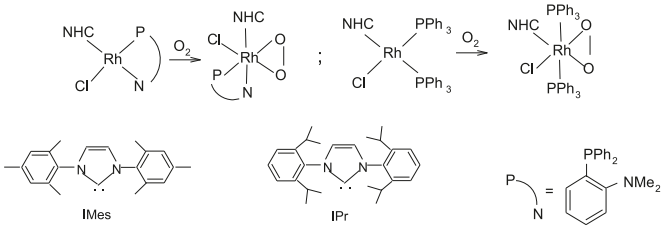
$C_{55}H_{64}N_2ClP_2Rh$, fw = 952.33, orange plate, size 0.20 mm × 0.25 mm × 0.50 mm, monoclinic, space group *P* 2$_1$/*n* (No. 14), *a* = 11.1595(6) Å, *b* = 20.971(1) Å, *c* = 20.938(1) Å, β = 95.693(2)°, *V* = 4875.8(5) Å^3, *Z* = 4, D_{calcd} = 1.299 g cm^{-3}, μ = 0.509 mm^{-1}. *F*(000) = 2000.00, 69 860 total reflections (11 679 independent of symmetry, 9737 for $I > 2\sigma(I)$), 558 variables; residuals (refined on F^2, all data): *R*1 = 0.037, *wR*2 = 0.067.

Crystal data for 9

$C_{57}H_{60}N_2ClP_2Rh{\cdot}0.5C_6H_6$, fw = 1011.32, orange plate, size 0.04 mm × 0.15 mm × 0.25 mm, triclinic, space group *P*-1 (No. 2), *a* = 12.6856(8) Å, *b* = 17.438(1) Å, *c* = 24.693(2) Å, α = 80.911(3)°, β = 81.812(2)°, γ = 86.156(3)°, *V* = 5333.1(6) Å^3, *Z* = 4, D_{calcd} = 1.256 g cm^{-3}, μ = 0.476 cm^{-1}. *F*(000) = 2116.00, 69 026 total reflections (18 891 independent of symmetry, 14 480 for $I > 2\sigma(I)$), 1200 variables, residuals (refined on F^2, all data): *R*1 = 0.061, *wR*2 = 0.103. The material crystallized with two molecules of the Rh-complex, one C_6H_6 molecule and one additional solvent molecule, in the asymmetric unit; the solvent

resembled hexane, but could not be modeled satisfactorily and was thus removed from the model, with the SQUEEZE program[11] used to correct data for any residual electron density found in the space formerly occupied by the solvent.

Scheme 1. Reactions of O_2 with some Rh–*N*-heterocyclic carbene (NHC)–phosphine complexes.



Reactivity of the complexes

The complexes (~0.05 mmol) were dissolved in C_6D_6 (1 mL), and a sample (~0.7 mL) of the solution was placed in a J-Young NMR tube and subjected to an atmosphere of O_2, CO, or H_2 at room temperature; $^{31}P\{^1H\}$ NMR spectral changes were then monitored.

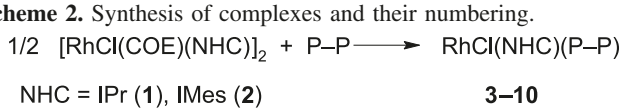
Results and discussion

Synthesis and spectroscopic characterization of complexes

The diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n =2, dppe; n = 4, dppb) and 1,2-bis(diphenylphosphino)benzene (dppbz) react at room temperature with $[RhCl(COE)(NHC)]_2$ complexes in benzene to give yellow RhCl(NHC)(P–P) species in 77%–96% isolated yields (NHC = IPr or IMes, and P–P is the chelating diphosphine). All eight complexes (**3**–**10**) have been synthesized (see Scheme 2) and well characterized by elemental analysis, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry and, for **3**, **7**, and **9**, by X-ray crystallography.

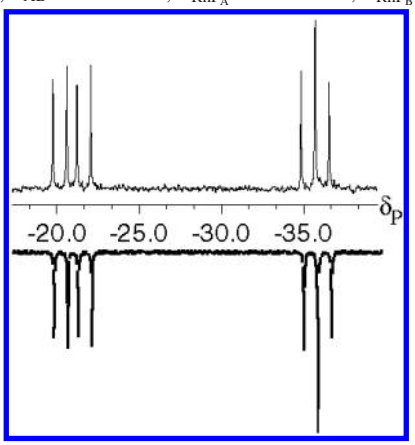
The solution NMR data for the complexes are generally straightforward, and most of the shifts are readily assigned based on previously reported data, for example, for *cis*-RhCl(NHC)$(PPh_3)_2$ and RhCl(NHC)(P–N) species (see Scheme 1).[5] All the complexes show a ^1H singlet for NC*H* between δ_H 6.79–6.89 and 6.21–6.29 for the IPr- and IMes-containing species, respectively. The IPr species **3**, **5**, and **9** show four sets of doublets for inequivalent IPr–Me groups, with coupling of ~6.7 Hz to a IPr–methine proton; the doublets indicate restricted rotation about the Rh–C bond or, less likely, the N_{imid}–C_{arene} bond.[12] Complex **7** shows broad signals for these methyls, presumably because of the relative greater flexibility of the dppb chelate ring, which might allow for more rotational motion.[13] The Me signals are sometimes shifted downfield (e.g., to δ_H 1.89 for **3**), which could result from a deshielding effect from a phenyl ring of the diphosphine (see the following section for the structure of **3**). The IPr–methine protons appear as two septets (for **3**), two multiplets (for **5**), or one broad singlet (for **7**). For each of the IMes species **4**, **6**, **8**, and **10**, the Me protons are seen as three singlets at δ_H ~2.8, ~2.2, and between 1.9 and 1.6, implying that the two *o*-Me groups on one aromatic ring are inequivalent, consistent again with some restricted rotation.

Scheme 2. Synthesis of complexes and their numbering.



NHC	dppm	dppe	dppb	dppbz
IPr	**3**	**5**	**7**	**9**
IMes	**4**	**6**	**8**	**10**

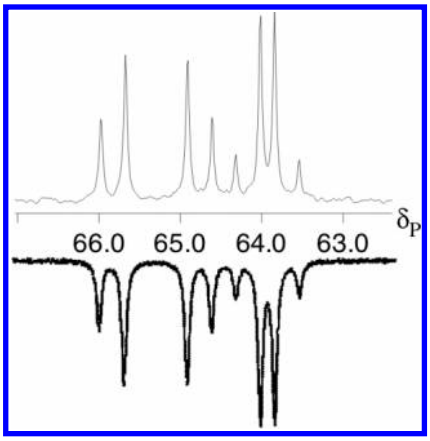
Fig. 1. The experimental (upper) and simulated (lower) $^{31}P\{^1H\}$ NMR spectra of RhCl(IPr)(dppm) (**3**). δ_{P_A} = –35.68, δ_{P_B} = –20.92, J_{AB} = 101.0 Hz, J_{RhP_A} = 104.0 Hz, J_{RhP_B} = 178.0 Hz.



The two singlets seen for the *m*-protons of the IMes ligand similarly imply inequivalence of these protons within one ring; the same description has been noted for the analogous *cis*-RhCl(IMes)$(PPh_3)_2$ complex.[4j] Where possible, we have assigned the *m*- and *p*-protons of the IPr ligand, the *m*-protons of the IMes ligand, and the phenyl protons of the PPh_2 groups, based on (*i*) expected splitting patterns (e.g., the *m*-H of IPr and of IMes are doublets and singlets, respectively, and the *p*-H of IPr is a triplet),[2,5,14] (*ii*) data for free IPr and IMes,[15], and (*iii*) data for the free diphosphines.[16] The more tentative assignments of these aromatic protons are indicated by a query (?) in the Experimental section. The CH_2 protons of the carbon backbone of the diphosphine ligand in **5**–**8** appear as a multiplet or broad singlets. Those of dppm in **3** and **4** are seen as a broadened triplet, which is in fact a set of overlapping doublets that result from two equivalent protons coupling to the two inequivalent P atoms; the ^{31}P-decoupled spectra showed a slightly broadened singlet.

The $^{31}P\{^1H\}$ NMR spectra reveal the expected inequivalent P atoms. For **5** and **7**–**9**, first-order spectra show doublets of doublets with J_{PP} values of 48–38 Hz and J_{RhP} values of 123–114 and 208–205 Hz (for the P atom cis and trans to Cl, respectively[4d,4e,5]). For the other complexes, the spectra are more complex ABX systems but are readily simulated. Figure 1 shows the data for **3** and those of **4** (the other dppm derivative) are very similar: the J_{PP} values are now ~100 Hz, with J_{RhP} values of ~100 and 180 Hz, respectively, for the P atoms cis and trans to Cl. The ABX spectra of **6** (Fig. 2) and **10** are similar to each other, with J_{PP} and

Fig. 2. The experimental (upper) and simulated (lower) $^{31}P\{^{1}H\}$ NMR spectra of RhCl(IMes)(dppe) (**6**) δ_{P_A} = –64.26, δ_{P_B} = –64.96, J_{AB} = 36.6 Hz, J_{RhP_A} = 125.7 Hz, J_{RhP_B} = 205.7 Hz.



J_{RhP} values close to those seen in the first-order spectra of **5** and **7**–**9**. Spectra akin to those of Fig. 2 have been noted previously for analogous *cis*-RhCl(IMes)$[P(OPh)_3]_2$ species.[4e]

The expected ddd pattern (coupling to Rh and inequivalent P atoms) in the $^{13}C\{^{1}H\}$ spectra for the Rh–*C* signals is seen at δ ~195 for **3**, **4**, and **9**, with J_{RhC} being ~125 Hz and the J_{PC} values being ~10 and ~50 Hz. For **5** and **10**, only somewhat broader dd patterns are seen, whereas for **6**–**8** these signals are not seen and are presumably broadened into the baseline by some exchange processes, reflecting a relatively labile Rh–carbene bond (see the last section on the reactivity toward CO); the flexibility of the dppb ring might account in part for the lack of the Rh–*C* signal in **7** and **8**. The non-appearance of carbene-carbon resonances in Rh–NHC species is not unusual.[2,4e,5] There is no question about the identity of the complexes, which are all essentially square-planar Rh(I) species, with some distortion induced by the chelating phosphines, as seen particularly in the structure of **3**, the dppm derivative (see the following section). For **3** and **4**, the $^{13}C\{^{1}H\}$ signal for the P*C*H_2P carbon is seen as a doublet of doublets at δ ~50 with J_{CP} values for the inequivalent P atoms in the 18–30 Hz range. For complexes **5**–**10**, $^{13}C\{^{1}H\}$ signals for the C atoms attached to P atoms are seen as doublets in the expected regions δ_C 25–36 and 125–139, respectively, for alkyl and aryl carbons; uncertain assignments are again indicated by ?.

Mass spectral data reveal the parent peak for all the complexes using either the EI mode (for **3**–**6**, **9**, and **10**) or the MALDI-TOF ion source (for **7** and **8**).

Structural characterization of 3, 7, and 9

The crystal structures of **3**, **7**, and **9** (all containing IPr) were established by X-ray analysis; the molecular structures and selected bond lengths and angles are shown in Figs. 3, 4, and 5, respectively. Complex **3** crystallized with one-half of a benzene molecule, whereas **9** crystallized as two independent molecules with one benzene molecule and one additional solvent molecule (likely hexane) in the asymmetric unit; **7** was nonsolvated. The essentially square-planar structures show some distortion, particularly in the dppm of **3** where the P1–Rh–P2 bond angle is 72.81° and the adjacent

Fig. 3. ORTEP diagram of RhCl(IPr)(dppm) (**3**) with 50% probability thermal ellipsoids; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1—C1, 2.067(2); Rh1—Cl1, 2.3793(6); Rh1—P1, 2.2005(6); Rh1—P2, 2.2516(6); P1—C28, 1.854(2); P2—C28, 1.845(2); C1–Rh1–Cl1, 90.30(6); Cl1–Rh1–P2, 93.94(2); P2–Rh1–P1, 72.81(2); P1–Rh1–C1, 103.07(6); C1–Rh1–P2, 175.28(6); Cl1–Rh1–P1, 166.32(2).

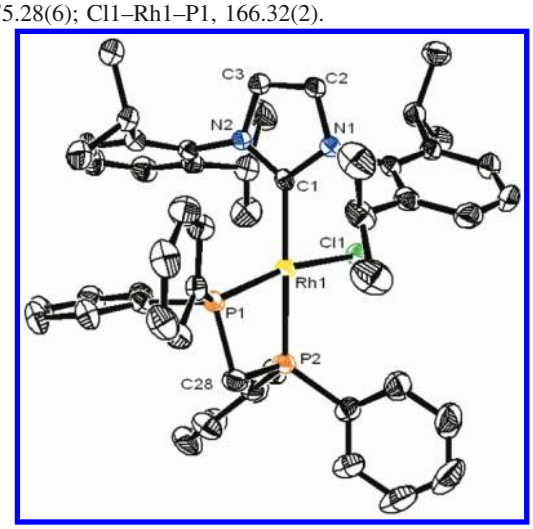
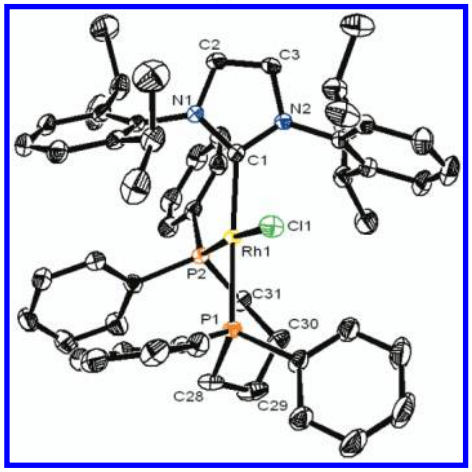
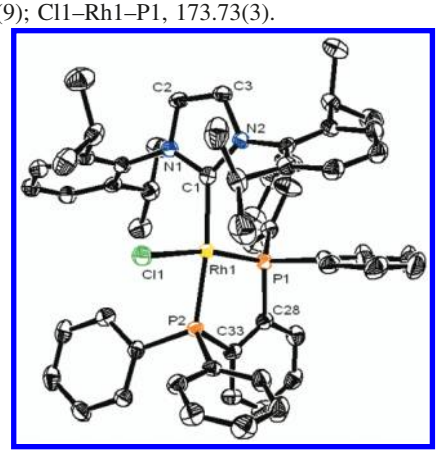


Fig. 4. ORTEP diagram of RhCl(IPr)(dppb) (**7**) with 50% probability thermal ellipsoids; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1—C1, 2.0484(15); Rh1—Cl1, 2.3846(4); Rh1—P1, 2.2888(4); Rh1—P2, 2.2043(4); P1—C28, 1.8427(18); P2—C31, 1.8681(16); C1–Rh1–Cl1, 86.01(4); Cl1–Rh1–P1, 82.569(15); P1–Rh1–P2, 91.046(15); P2–Rh1–C1, 100.39(4); C1–Rh1–P1, 168.34(4); Cl1–Rh1–P2, 173.587(15).



Cl1–Rh1–P2 and P1–Rh1–C1 bond angles are 93.94 and 103.07(6)°, respectively. In **7**, the more flexible dppb allows for a P1–Rh–P2 bond angle of 91.05°. Steric interactions between the IPr and a PPh_2–phenyl ring are evident in all three structures, this accounting for cis C–Rh–P angles of ~100°. The Rh–C and Rh–Cl bond lengths are in the established range for such chloro(carbene)–Rh(I or III) complexes.[2,5,4d,17–21] In all three complexes, the Rh–P bond trans to the carbene is 0.04–0.08 Å longer than the one cis to the carbene, a finding compatible with data for *cis*-RhCl(IMes)$(PPh_3)_2$, where the difference is about 0.09 Å.[4d] Our data also agree with a finding from Crudden's group that

Fig. 5. ORTEP diagram of RhCl(IPr)(dppbz) (**9**) with 50% probability thermal ellipsoids; the other independent molecule in the asymmetric unit, and H atoms, are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1—C1, 2.101(3); Rh1—Cl1, 2.3929(8); Rh1—P2, 2.2239(8); Rh1—P1, 2.1796(9); P1—C28, 1.852(3); P2—C33, 1.832(3); C1–Rh1–Cl1, 91.58(8); Cl1–Rh1–P2, 83.92(3); P2–Rh1–P1, 85.30(3); P1–Rh1–C1, 99.66(8); C1–Rh1–P2, 173.14(9); Cl1–Rh1–P1, 173.73(3).



Rh–P bonds in *cis*-RhCl(NHC)$(PPh_3)_2$ complexes are marginally shorter (by up to 0.03 Å) than corresponding bonds in $RhCl(PPh_3)_3$ and *trans*-RhCl(CO)$(PPh_3)_2$;[4d] in the case of RhCl(IPr)(dppbz) (**9**), the difference is up to 0.08 Å. Data from Herrmann's group on other chloro(carbene)phosphine–phosphite–Rh(I) complexes[18] also support this finding, which is likely general within analogous Rh–carbene and Rh–phosphine species.

Reactivity of the complexes

Complexes **3**–**10** are all highly soluble in benzene, toluene, CH_2Cl_2, $CHCl_3$, and polar aprotic solvents, but are insoluble in solvents such as hexane. In the solid state, these complexes are air-stable, but in solution (e.g., in C_6H_6/C_6D_6), they are sensitive to air or oxygen and rapidly decompose at room temperature with formation of free diphosphine dioxide, as demonstrated by in situ $^{31}P\{^1H\}$ NMR data; singlets were seen at δ_P = 24.4, 12.2, 31.7, and 32.0, respectively, for the dioxides of dppm, dppe, dppb, and dppbz, in agreement with literature data,[22,23] and were identical to values measured by in situ oxidation of the free diphosphine in C_6D_6 with H_2O_2. The reactivity toward O_2 of these diphosphine complexes is markedly different to that of the analogous *cis*-RhCl(NHC)$(PPh_3)_2$ complex, which under the same conditions undergoes irreversible oxidative addition to form a Rh(III)–peroxide that contains, however, *trans*-PPh_3 ligands (see Scheme 1)[5]; this peroxide is stable in both the solid state, and even in solution shows no sign of decomposition to $OPPh_3$ over 24 h in air.[5] The necessarily cis-chelating diphosphines clearly do not allow for formation at ambient conditions of a stable peroxide, although the chelated P–N ligand mentioned in the Introduction (Scheme 1) does so.[5] Whether oxidation of the diphosphines occurs via an intermediate with coordinated O_2 requires detailed low-temperature studies. Loss of a chelating diphosphine as the dioxide during oxygenation of a Rh(I)–tris(pyrazolyl)borate–dppe complex in solution in attempts to study formation of peroxide species has been demonstrated previously,[22] although the chelating diphosphine ligands are retained when $Rh(dppm)_2^+$ and $Rh(dppe)_2^+$ react in solution with O_2 at ambient conditions to form the respective *cis*-Rh(P–P)$_2(O_2)^+$ peroxide species, where (P–P) is the chelating diphosphine.[13b] Our findings at this stage on the reactivity of O_2 toward the RhCl(NHC)(P–P) complexes unfortunately cannot contribute to the question of the nature of the coordinated O_2 in Rh–NHC complexes with and without an ancillary phosphine ligand, in which singlet oxygen has been suggested (see Introduction).[3,4a] Studies on such systems are ongoing.

Reaction of a benzene solution of RhCl(NHC)(dppe) [NHC = IPr (**5**), IMes (**6**)] with CO at ambient conditions rapidly precipitated a yellow solid, which was recrystallized by layering of a CH_2Cl_2 solution of the compound with hexane. The material, however, was shown by elemental analysis and $^{31}P\{^1H\}$ NMR and IR spectroscopies to be the known compound RhCl(CO)(dppe).[24,25] Reactions of CO with the dppm and dppb analogues (complexes **3**, **4**, **7**, and **8**) also resulted in displacement of the NHC ligand by CO as shown by in situ ^1H NMR, when resonances of the free carbenes were generated.[26]

The Rh products were not investigated, but are presumed to be the well-known dimeric, bridged-diphosphine complexes *trans*-$[RhCl(CO)]_2(\mu$-P–P$)_2$ that are formed with dppm and dppb.[25] The substitution of an NHC ligand by CO, to the best of our knowledge, has not been reported, and implies a relatively labile NHC ligand; indeed, substitution of IMes by PPh_3 has been reported (see the following).[3,4f] Within Rh–NHC–carbonyl systems, $RhCl(CO)(NHC)_2$[2,14,27] and $RhCl(CO)_2(NHC)$[2,19,28] complexes have been synthesized by reacting CO with Rh–NHC precursors, whereas RhCl(CO)(PPh_3)(NHC) has been made from $RhCl(PPh_3)_2$(NHC) and CO.[3,4d,4f,4j]

The RhCl(NHC)(P–P) complexes in benzene solution do not react with H_2 at ambient conditions. Known hydrido complexes of the type $Rh(H)_2Cl(NHC)_2$ and $[Rh(H)_2Cl(NHC)]_2$ have been made by reaction of H_2 with Rh(I)–NHC precursors,[2,3,14,27] whereas Rh–hydrido–NHC species have also been generated via intramolecular C–H activation of the Me group of IMes.[14,29] Hydrido derivatives of Rh–NHC–phosphine species have not yet been reported.

Supplementary data

Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Building M-55, 1200 Montreal Road, Ottawa, ON K1A 0R6, Canada. DUD 3999. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/eng/ibp/cisti/collection/unpublished-data.html. CCDC numbers 739246–739248 contain the crystallographic data for complexes **3**, **7**, and **9**, respectively. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac/uk).

Acknowledgment

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

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