Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 8715

www.rsc.org/dalton

PAPER

C–Cl bond activation of *ortho*-chlorinated benzamides by nickel and cobalt compounds supported with phosphine ligands†

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Received 12th December 2011, Accepted 28th May 2012
DOI: 10.1039/c2dt12395a

The C–Cl bonds of *ortho*-chlorinated benzamides Cl-*ortho*-$C_6H_4C(=O)NHR$ (R = Me (**1**), *n*Bu (**2**), Ph (**3**), (4-Me)Ph (**4**) and (4-Cl)Ph (**5**)) were successfully activated by tetrakis(trimethylphosphine)nickel(0) and tetrakis(trimethylphosphine)cobalt(0). The four-coordinate nickel(II) chloride complexes *trans*-$[(C_6H_4C(=O)NHR)Ni(PMe_3)_2Cl]$ (R = Me (**6**), *n*Bu (**7**), Ph (**8**) and (4-Me)Ph (**9**)) as C–Cl bond activation products were obtained without coordination of the amide groups. In the case of **2**, the ionic penta-coordinate cobalt(II) chloride $[(C_6H_4C(=O)NHnBu)Co(PMe_3)_3]Cl$ (**10**) with the $[C_{phenyl}, O_{amide}]$-chelate coordination as the C–Cl bond activation product was isolated. Under similar reaction conditions, for the benzamides **3–5**, hexa-coordinate bis-chelate cobalt(III) complexes $(C_6H_4C(=O)NHR)Co(Cl\text{-}ortho\text{-}C_6H_4C(=O)NR)(PMe_3)_2$ (**11–13**) were obtained *via* the reaction with $[Co(PMe_3)_4]$. Complexes **11–13** have both a five-membered [*C*,*N*]-coordinate chelate ring and a four-membered [*N*,*O*]-coordinate chelate ring with two trimethyphosphine ligands in the axial positions. Phosphonium salts $[Me_3P^+\text{-}ortho\text{-}C_6H_4C(=O)NHR]Cl^-$ (R = Ph (**14**) and (4-Me)Ph (**15**)) were isolated by reaction of complexes **8** and **9** as a starting material under 1 bar of CO at room temperature. The crystal and molecular structures of complexes **6**, **7** and **9–12** were determined by single-crystal X-ray diffraction.

1. Introduction

Chloroarenes play an important role in many fields, especially in industry and agriculture. At the same time, the application of them also leads to environmental problems. They are commonly found as soil and groundwater contaminants because most of them are toxic and thermally stable.[1] How to cope with these issues has driven several research groups to examine practical and effective methods to transform toxic and inert chloroarenes into useful and/or environment-friendly substances. Activation of the comparatively inert C–Cl bond seems to be a feasible approach using transition metal complexes under stoichiometric or catalytic conditions.[2] Related studies could be found in cross-coupling reactions such as Heck reaction, Suzuki coupling and Stille coupling. Catalytic activation of the C–Cl bond by palladium,[3] nickel,[4] cobalt,[5] rhodium[6] and iron[7] complexes is the key step in these reactions.

We reported C–Cl bond activation at a cobalt(I), iron (0) and nickel(0) center with imine as an anchoring group through cyclometalation reactions.[8–10] Novel *ortho*-chelated cobalt(III) complexes were obtained through reactions of *ortho*-chlorinated aromatic compounds bearing imine groups as anchoring groups with cobalt(I) complexes, $[CoMe(PMe_3)_4]$, $[CoCl(PMe_3)_3]$ or $[CoBr(PMe_3)_3]$, by activation of the C–Cl bond.[8] Reactions of mono- and di-*ortho*-chlorinated compounds containing imine groups as directing groups with $Fe(PMe_3)_4$ delivered cyclometalated complexes in octahedral coordination geometry *via* the C–Cl bond activation.[9] The reaction of *ortho*-chlorinated phenylimine with tetrakis(trimethylphosphine)nickel(0) under a CO atmosphere (1 bar) at room temperature provides bis(isoindolinones) *via* carbonylative cyclization and dimerization through C–Cl bond cleavage.[10]

As a part of our continuing interest in the C–Cl bond activation of chlorinated aromatic molecules, we prefer to produce the C–Cl bond activation product through cyclometalation reactions with an *ortho*-chlorinated benzamide-O atom or N atom as an anchoring group, by nickel(0) and cobalt(0) complexes supported with phosphine ligands. The C–Cl bond of the *ortho*-chlorinated benzamides **1–5** were successfully activated by tetrakis(trimethylphosphine)nickel(0) and tetrakis(trimethylphosphine)cobalt(0). The four-coordinate nickel(II) chloride complexes (**6–9**) as C–Cl bond activation products were obtained. In the case of benzamide **2**, the cobalt(II) chloride **10** as a C–Cl bond activation product was isolated. Instead of the *n*-butyl group on the amide-N atom, if the substituent on the amide-N atom is phenyl or its derivatives, the hexa-coordinate bis-chelate cobalt(III) complexes **11–13** could be obtained *via* the reaction of the amides **3–5** with $[Co(PMe_3)_4]$. The phosphonium salts **14** and **15** were isolated by reaction of complexes **3** and **4** as starting material under 1 bar of CO at room temperature. The crystal and molecular structures of complexes **6**, **7** and **9–12** were determined by single-crystal X-ray diffraction.

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†CCDC 806080–806085. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12395a

2. Experimental section

2.1 General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Literature methods were used in the preparation of $Ni(PMe_3)_4$[11a] and $Co(PMe_3)_4$.[11b] *ortho*-Chlorinated benzamides were obtained by refluxing mixtures of *ortho*-chlorobenzoyl chloride and amine in diethyl ether solution. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on an ALPHA FT-IR Spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra (300, 75, and 121 MHz, respectively) were recorded on a Bruker Avance 300 spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broadband proton decoupling. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

2.2 Syntheses

Synthesis of 6. A solution of **1** (0.39 g, 2.34 mmol) in 30 mL of THF was combined with a solution of $Ni(PMe_3)_4$ (0.85 g, 2.34 mmol) in THF (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned brown-yellow in color. After filtering, the yellow-brown residue was extracted with pentane (40 mL) and diethyl ether (50 mL), respectively. Repeated re-crystallization from diethyl ether at 4 °C yielded yellow crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.57 g (64%). m.p.: >136 °C. Analysis for **6**, $C_{14}H_{26}ClNNiOP_2$ (380.44 g mol^{-1}), found (calcd): C, 44.15 (44.20); H, 6.78 (6.89); N, 3.70 (3.68)%. IR (Nujol mull): 3400 ν(N–H), 1626 ν(C═O), 946 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 297 K, ppm): δ 8.06 (br, 1H, N*H*), 6.81 (t, ^3J(HH) = 7.4 Hz, 1H, Ar–*H*), 6.88 (t′, ^3J(HH) = 7.2 Hz, 1H, Ar–*H*), 7.66 (d, ^3J(HH) = 7.5 Hz, 1H, Ar–*H*), 7.86 (d, ^3J(HH) = 9 Hz, 1H, Ar–*H*), 2.94 (d, ^3J(HH) = 4.8 Hz, 3H, CH_3), 0.77 (t′, $|^2J(PH) + {}^4J(PH)|$ = 7.8 Hz, 18H, PCH_3). ^{13}C NMR (75 MHz, C_6D_6, 297 K, ppm): δ 169.3 (s, *C*═O), 121.8–135.0 (s, C_{arom}), 23.0 (s, 3H, *C*H_3) 12.7 (t, $|^1J(PC) + {}^3J(PC)|$ = 27.8 Hz, P*C*H_3). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K, ppm): δ −13.1 (s, *P*CH_3).

Synthesis of 7. A solution of **2** (0.42 g, 1.98 mmol) in 30 mL of THF was combined with a solution of $Ni(PMe_3)_4$ (0.72 g, 1.98 mmol) in THF (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned brown-yellow in color. After filtering, the yellow-brown residue was extracted with pentane (40 mL) and diethyl ether (50 mL). Repeated re-crystallization from pentane at 4 °C yielded yellow crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.57 g (68%). m.p.: >109 °C. Analysis for **7**, $C_{17}H_{32}ClNNiOP_2$ (422.54 g mol^{-1}), found (calcd): C, 48.52 (48.32); H, 7.60 (7.63) ; N, 3.29 (3.31)%. IR (Nujol mull): 3283 ν(N–H), 1651 ν(C═O), 947 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 297 K, ppm): δ 8.57 (br, 1H, N*H*), 8.02 (dd, 1H, ^3J(HH) = 7.8 Hz, ^4J(HH) = 1.5 Hz, Ar–*H*), 7.65 (d, 1H, ^3J(HH) = 7.8 Hz, Ar–*H*), 6.90 (dt′, 1H, ^3J(HH) = 6 Hz, ^4J(HH) = 1.8 Hz, Ar–*H*), 6.83 (dt′, 1H, ^3J(HH) = 7.2 Hz, ^4J(HH) = 1.5 Hz, Ar–*H*), 3.62 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.88 (t, 3H, ^3J(HH) = 7.5 Hz, CH_3), 0.78 (t′, 18H, $|^2J(PH) + {}^4J(PH)|$ = 7.8 Hz, PCH_3). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K, ppm): δ −13.3 (s, *P*CH_3).

Synthesis of 8. A solution of **3** (0.50 g, 2.14 mmol) in 30 mL of THF was combined with a solution of $Ni(PMe_3)_4$ (0.78 g, 2.14 mmol) in THF (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned yellow-brown in color. After filtering, the yellow-brown residue was extracted with pentane (40 mL) and diethyl ether (50 mL), respectively. Repeated re-crystallization from diethyl ether at 4 °C yielded red-brown crystals. Yield: 0.60 g (64%). m.p.: >136 °C. Analysis for **8**, $C_{19}H_{28}ClNNiOP_2$ (442.53 g mol^{-1}), found (calcd): C, 51.42 (51.57); H, 6.29 (6.38); N, 3.00 (3.17)%. IR (Nujol mull): 3302 ν(N–H), 1631 ν(C═O), 937 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 297 K, ppm): δ 12.8 (s, 1H, N*H*), 8.67 (m, 3H, Ar–*H*), 7.66 (m, 1H, Ar–*H*), 7.30 (m, 2H, Ar–*H*), 6.96 (m, 1H, Ar–*H*), 6.87 (m, 2H, Ar–*H*), 0.67 (t′, $|^2J(PH) + {}^4J(PH)|$ = 7.8 Hz, 18H, PCH_3). ^{13}C NMR (75 MHz, C_6D_6, 297 K. ppm): δ 165.6 (s, *C*═O), 119.4–140.5 (s, C_{arom}), 12.3 (t, $|^1J(PC) + {}^3J(PC)|$ = 28.6 Hz, P*C*H_3). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K, ppm): δ −12.33 (s, *P*CH_3).

Synthesis of 9. A solution of **4** (0.43 g, 1.76 mmol) in 30 mL of THF was combined with a solution of $Ni(PMe_3)_4$ (0.64 g, 1.76 mmol) in THF (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 30 h. During this period the pale yellow mixture turned brown-yellow in color. After filtering, the yellow-brown residue was extracted with pentane (40 mL) and diethyl ether (50 mL), respectively. Repeated re-crystallization from diethyl ether at 4 °C yielded yellow crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.50 g (61%). m.p.: >145 °C. Analysis for **9**, $C_{20}H_{30}ClNNiOP_2$ (456.53 g mol^{-1}), found (calcd): C, 56.58 (56.61); H, 6.60 (6.62); N, 3.22 (3.07)%. IR (Nujol mull): 3458 ν(N–H), 1651 ν(C═O), 946 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 297 K, ppm): δ 12.72 (s, 1H, N*H*), 8.68 (dd, 1H, ^3J(HH) = 6.9 Hz, ^4J(HH) = 2.7 Hz, Ar–*H*), 8.60 (d, 2H, ^3J(HH) = 8.4 Hz, Ar–*H*), 7.65 (dd, 1H, ^3J(HH) = 6.3 Hz, ^4J(HH) = 2.1 Hz, Ar–*H*), 7.09 (m, 2H, Ar–*H*), 6.89 (m, 2H, Ar–*H*), 2.10 (s, 3H, CH_3), 0.68 (t′, 18H, $|^2J(PH) + {}^4J(PH)|$ = 7.6 Hz, PCH_3). ^{13}C NMR (75 MHz, C_6D_6, 297 K, ppm): δ 165.6 (s, *C*═O), 119.4–138.1 (s, C_{arom}), 20.8 (s, *C*H_3), 12.3 (t, $|^1J(PC) + {}^3J(PC)|$ = 29.4 Hz, P*C*H_3). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K, ppm): δ −12.3 (s, *P*CH_3).

Synthesis of 10. A solution of **2** (0.42 g, 1.98 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (0.72 g, 1.98 mmol) in 20 mL of THF at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. During this period the yellow-brown mixture turned red-brown in color. After filtering, the red-brown residue was extracted with diethyl ether (50 mL). Repeated re-crystallization from diethyl ether at −12 °C yielded red crystals. Yield: 0.36 g (36%). m.p.: >148 °C. Analysis for **10**, $C_{20}H_{41}ClCoNOP_3$ (498.83 g mol^{-1}), found (calcd): C, 47.80 (48.16); H, 8.30 (8.28) %. IR (Nujol mull): 3229 ν(N–H), 1595 ν(C═O), 941 $\rho(PMe_3)$ cm^{-1}.

Synthesis of 11. A solution of **3** (0.80 g, 3.48 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (0.63 g, 1.74 mmol) in 20 mL of THF at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. During this period the yellow-brown mixture turned red-brown in color. After filtering, the red-brown residue was extracted with diethyl ether (50 mL). Repeated re-crystallization from diethyl ether at −12 °C yielded red crystals. Yield: 0.91 g (82%). m.p.: >142 °C. Analysis for **11**, $C_{32}H_{36}ClCoN_2O_2P_2$ (636.95 g mol^{-1}), found (calcd): C, 60.70 (60.34); H, 5.88 (5.70) %. IR (Nujol mull): 1608 ν(C═O), 944 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 298 K, ppm): δ 6.74–8.85 (m, 18H, Ar–*H*), 0.80–1.02 (m, 18H, PCH_3). ^{31}P NMR (121.5 MHz, C_6D_6, 298 K, ppm): δ 4.3 (s, *P*CH_3).

Synthesis of 12. A solution of **4** (0.65 g, 2.51 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (0.46 g, 1.25 mmol) in 20 mL of THF at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. During this period the yellow-brown mixture turned red-brown in color. After filtering, the red-brown residue was extracted with diethyl ether (50 mL). Repeated re-crystallization from diethyl ether at −12 °C yielded red crystals. Yield: 0.67 g (80%). m.p.: >184 °C. Analysis for **12**, $C_{34}H_{40}ClCoN_2O_2P_2$ (665.0 g mol^{-1}), found (calcd): C, 61.20 (61.41); H, 6.31 (6.06) %. IR (Nujol mull): 1607 ν(C═O), 947 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 298 K, ppm): δ 6.62–8.36 (m, 16H, Ar–*H*), 1.90–2.49 (m, 6H CH_3), 0.74–0.91 (m, 18H, PCH_3). ^{31}P NMR (121.5 MHz, C_6D_6, 298 K, ppm): δ 4.4 (t, *P*CH_3).

Synthesis of 13. A solution of **5** (0.65 g, 2.46 mmol) in 30 mL of THF was combined with a solution of $Co(PMe_3)_4$ (0.45 g, 1.23 mmol) in 20 mL of THF at −78 °C. The reaction mixture was warmed to ambient temperature and stirred for 16 h. During this period the yellow-brown mixture turned red-brown in color. After filtering, the red-brown residue was extracted with diethyl ether (50 mL). Repeated re-crystallization from diethyl ether at −12 °C yielded red crystals. Yield: 0.50 g (88%). m.p.: >190 °C. Analysis for **13**, $C_{32}H_{34}Cl_3CoN_2O_2P_2$ (705.93 g mol^{-1}), found (calcd): C, 54.63 (54.45); H, 4.59 (4.85)%. IR (Nujol mull): 1596 ν(C═O), 947 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 298 K, ppm): δ 6.47–8.42 (m, 16H, Ar–*H*), 0.74–0.88 (m, 18H, PCH_3). ^{31}P NMR (121.5 MHz, C_6D_6, 298 K, ppm): δ 5.2 (s, *P*CH_3).

Synthesis of 14. A solution of **8** (1.26 g, 2.8 mmol) in 40 mL of diethyl ether was stirred under 1 bar of CO at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 24 h. During this period the brown mixture turned single yellow, and a great deal of white powder was obtained. The white powder was washed by diethyl ether. Yield: 0.74 g (85%). m.p.: >89 °C. $(M - Cl)^+$ = 272.1. Analysis for **14**, $C_{16}H_{19}ClNOP$ (307.75 g mol^{-1}), found (calcd): C, 62.69 (62.44); N, 4.22 (4.55); H, 6.47 (6.22)%. IR (Nujol mull): 3508 ν(N–H), 1650 ν(C═O), 968 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, D_2O, 297 K, ppm): δ 7.29–8.00 (m, 9H, Ar–*H*), 2.15 (d, $^2J_{PH}$ = 14.1 Hz, 9H, PCH_3). ^{31}P NMR (121.5 MHz, D_2O, 294 K, ppm): δ 48.8 (s, *P*CH_3).

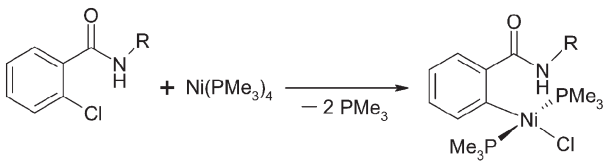
Synthesis of 15. A solution of **9** (1.36 g, 2.97 mmol) in 40 mL of diethyl ether was stirred under 1 bar of CO at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 24 h. During this period the brown mixture turned single yellow, and a great deal of white powder was obtained. The white powder was washed by diethyl ether. Yield: 0.84 g (88%). m.p.: >119 °C. $(M - Cl)^+$ = 286.1. Analysis for **15**, $C_{17}H_{21}ClNOP$ (321.78 g mol^{-1}), found (calcd): C, 63.79 (63.45); N, 4.32(4.35); H, 6.50 (6.58)%. IR (Nujol mull): 3388 ν(N–H), 1656 ν(C═O), 954 $\rho(PMe_3)$ cm^{-1}. ^1H NMR (300 MHz, D_2O, 297 K, ppm): δ 7.10–7.86 (m, 8H, Ar–*H*), 2.14 (s, 3H, CH_3), 1.97 (d, $^2J_{PH}$ = 14.1 Hz, 9H, PCH_3). ^{31}P NMR (121.5 MHz, D_2O, 294 K, ppm): δ 22.8 (s, *P*CH_3).

X-Ray structure determinations. Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystallographic data for complexes **6**, **7** and **9–12** are summarized in Table 1. The structures were solved by direct methods and refined with the full-matrix least-squares method on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic. CCDC 806080 (**6**), 806081 (**7**), 806084 (**9**), 806082 (**10**), 806083 (**11**) and 806085 (**12**) contain the supplementary crystallographic data for this paper.†

3. Results and discussion

3.1. Reaction of [Ni (PMe_3)$_4$] with *ortho*-chlorinated benzamides

The reaction of *ortho*-chlorinated benzamides **1–4** with $Ni(PMe_3)_4$ afforded four-coordinate Ni(II) complexes **6–9** *via* C–Cl bond activation (eqn (1)).



(1)

1 - 4 **6 - 9**

R = Me nBu Ph (4-Me)Ph
1 2 3 4
6 7 8 9

Complexes **6–9** were isolated as crystals in yields of 64–68%. Complexes **6–9** were characterized by elemental analysis, IR and NMR spectroscopy. In the infrared spectra of complexes **6–9** the characteristic ν(C═O) bands were recorded at 1626, 1651, 1631 and 1651 cm^{-1}, while the corresponding ν(C═O) bands of the free *ortho*-chlorinated benzamides ligands (**1–4**) are located at 1650, 1659, 1643, 1659 cm^{-1}. The characteristic ν(N–H) band changes from 3287 to 3400 cm^{-1}. These substantial red shifts upon coordination of the C═O and N-donor atoms indicate a weakening of these bonds.

In the ^1H NMR spectra, the proton resonances of the N–H groups in complexes **6–9** are recorded as a singlet between 8.06 and 12.77 ppm, while those of the free ligands are at 8.18–10.80 ppm. Only one ^{31}P NMR signal is observed between −13.1 and −12.3 ppm as a singlet. This suggests that the two phosphorus atoms are in *trans*-orientation. Spectroscopic data

Table 1 Crystallographic data for complexes **6**, **7** and **9–12**

	6	**7**	**9**	**10**	**11**	**12**
Empirical formula	$C_{14}H_{26}ClNNiOP_2$	$C_{17}H_{32}ClNNiOP_2$	$C_{20}H_{30}ClNNiOP_2$	$C_{20}H_{41}ClCoNOP_3$	$C_{32}H_{36}ClCoN_2O_2P_2$	$C_{34}H_{40}ClCoN_2O_2P_2$
Fw	380.44	422.54	456.53	498.83	636.95	665.00
Crystal size/mm	0.15 × 0.10 × 0.10	0.15 × 0.15 × 0.10	0.28 × 0.25 × 0.20	0.15 × 0.15 × 0.10	0.15 × 0.15 × 0.10	0.28 × 0.25 × 0.20
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*Pbca*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a/Å	13.607(2)	9.6040(19)	13.506(3)	16.4434(11)	10.989(2)	9.9389(6)
b/Å	24.405(4)	19.709(4)	14.564(3)	9.1090(6)	14.336(3)	28.7709(17)
c/Å	16.845(3)	22.573(5)	12.115(2)	18.6041(13)	19.780(4)	11.8115(7)
α (°)	90	90	90	90	90	90
β (°)	91.232(3)	90	106.80(3)	108.4464(10)	93.90(3)	93.90(3)
γ (°)	90	90	90	90	90	90
V/Å^3	5592.9(16)	4272.7(15)	2281.3(8)	2643.4(3)	3108.1(11)	3343.5(3)
Z	12	8	4	4	4	4
D_{calcd}/g cm^{-3}	1.355	1.314	1.329	1.253	1.361	1.321
No. of rflns collected	26 057	18 755	10 503	14 855	23 633	17 944
No. of independent rflns	9255	4417	4562	5754	6313	6570
R_{int}	0.0633	0.0609	0.0606	0.0414	0.0237	0.0400
θ_{max} (°)	24.45	26.73	26.70	27.12	26.80	26.00
R_1 ($I > 2\sigma(I)$)	0.0633	0.0389	0.0424	0.0475	0.0357	0.0675
wR_2 (all data)	0.1814	0.1141	0.1174	0.1318	0.0921	0.1953

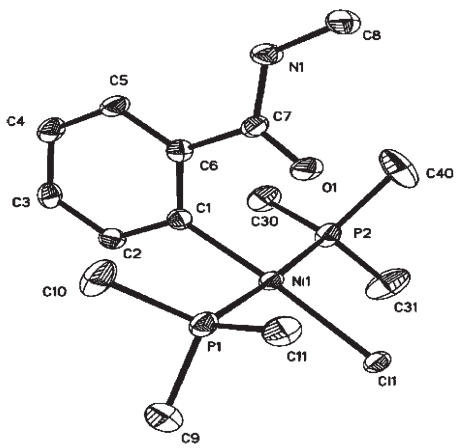


Fig. 1 Molecular structure of **6** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): Ni1–C1 1.883(6), Ni1–P1 2.1909(1), Ni1–P2 2.2035(1), Ni1–Cl1 2.2570(1), O1–C7 1.219(7), C7–N1 1.358(8), N1–C8 1.453(8); C1–Ni1–P1 89.72(18), C1–Ni1–P2 87.02(18), P1–Ni1–P2 175.76(8), C1–Ni1–Cl1 175.63(19), P1–Ni1–Cl1 90.05(7), P2–Ni1–Cl1 93.41(7).

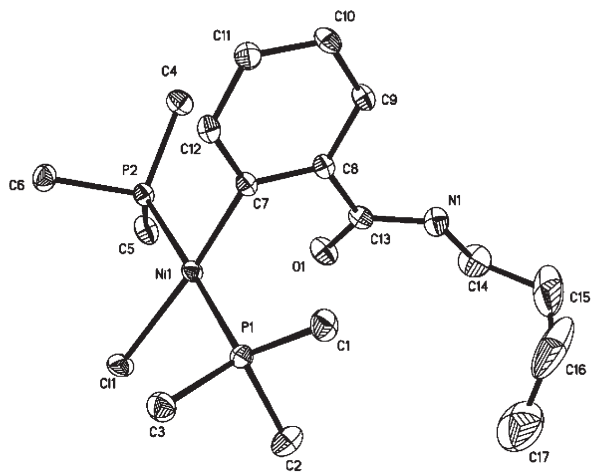


Fig. 2 Molecular structure of **7** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): O1–C13 1.238(3), N1–C13 1.343(4), N1–C14 1.455(4), Ni1–C7 1.885(2), Ni1–P2 2.1868(7), Ni1–P1 2.1887(7), Ni1–Cl1 2.2412(7); C7–Ni1–P2 88.45(7), C7–Ni1–P1 91.91(7), P2–Ni1–P1 177.67(3), C7–Ni1–Cl1 174.25(8), P2–Ni1–Cl1 90.12(3), P1–Ni1–Cl1 89.30(3).

are otherwise in accordance with the expected molecular configurations and are comparable with those in the literature.[10]

The molecular structures of complexes **6**, **7** and **9** are shown in Fig. 1–3. The selected bond distances and angles are listed under the figures. The complexes show distorted square planar structures with two *trans*-phosphine ligands. This is consistent with the observation in the ^{31}P NMR spectra. The nickel atom is centered in a square planar geometry with the *trans*-orientated Cl and phenyl-C atoms due to the *trans*-effect. The C–O distances (1.224(3), 1.238(3) and 1.219(7) Å for **6**, **7** and **9**) are in the region of a C=O double bond. This also implies that there is no bonding interaction between the O atom and the central nickel atom. In addition, the coordination of the N atom to the nickel atom does not exist because the distances between both atoms are much larger than those of the normal coordination bond of Ni–N (1.861–1.981 Å).[12] Therefore, treatment of $[Ni(PMe_3)_4]$ with **1–4** produced the coordinately unsaturated four-coordinate nickel(II) chloride complexes **6–9**. The expected cyclometalation reactions with an *ortho*-chlorinated benzamide-O atom or -N atom as an anchoring group did not occur. The possible explanation is that most of the nickel(II) complexes are apt to form square planar coordination geometry and the amide-N atom has weak coordination ability in comparison with the imine-N atom.

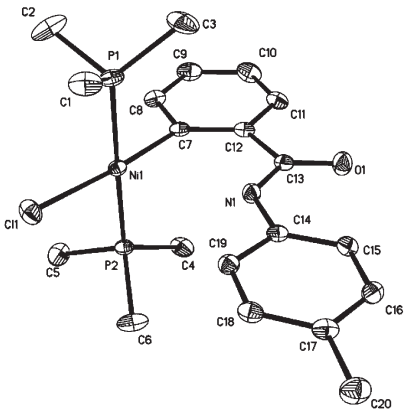


Fig. 3 Molecular structure of **9** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): Ni1–C7 1.895(2), Ni1–P1 2.1992(8), Ni1–P2 2.2012(7), Ni1–Cl1 2.2096(7), O1–C13 1.224(3), N1–C13 1.363(3), N1–C14 1.417(3); C7–Ni1–P1 88.17(7), C7–Ni1–P2 88.91(7), P1–Ni1–P2 176.66(3), C7–Ni1–Cl1 172.91(7), P1–Ni1–Cl1 92.29(3), P2–Ni1–Cl1 90.42(3).

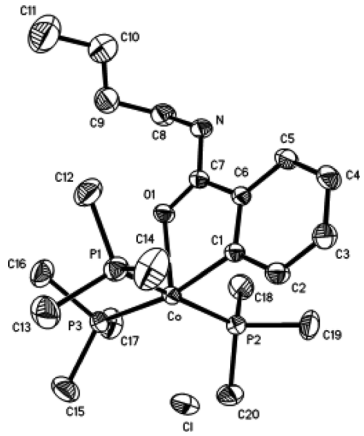


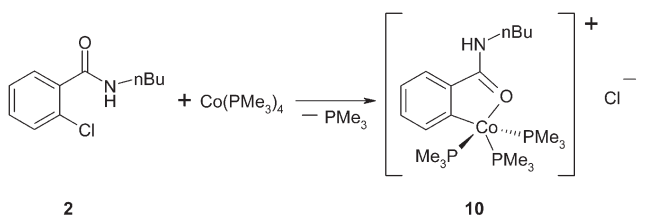
Fig. 4 Molecular structure of **10** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): Co–C1 1.957(3), Co–O1 2.228(2), Co–P1 2.2380(10), Co–P2 2.2422(10), Co–P3 2.2572(9); C1–Co–O1 80.27(10), C1–Co–P1 84.31(10), O1–Co–P1 94.91(7), C1–Co–P2 86.62(10), O1–Co–P2 93.33(7), P1–Co–P2 166.54(4), C1–Co–P3 166.54(9), O1–Co–P3 86.32(6), P1–Co–P3 95.78(4), P2–Co–P3 95.36(4).

In other words, an amide group is not a good anchoring group for cyclometallation.

It was found that the amide-O atoms in complexes **6** and **7** have different orientations from that of the amide-O atom in complex **9**. It is considered that there are weak coordination interactions between the oxygen atoms and the nickel centers in **6** and **7** (**6**: Ni1–O1 = 2.686 Å; **7**: Ni1–O1 = 2.856 Å), while a hyperconjugation between the phenyl group in one molecule of **9** and a methyl group of the trimethylphosphine ligand of another molecule of **9** in the crystal cell of **9** exists. It can also be understood as a result of crystal packing effect. In all of the three crystal lattices (**6**, **7** and **9**) no hydrogen bond related to the amide group was observed.

3.2. Reaction of $[Co(PMe_3)_4]$ with *ortho*-chlorinated benzamides

The reaction of N-*n*butyl-*ortho*-chlorinated benzamide **2** with $Co(PMe_3)_4$ afforded the cobalt(II) chloride complex **10** *via* C–Cl bond activation (eqn (2)).



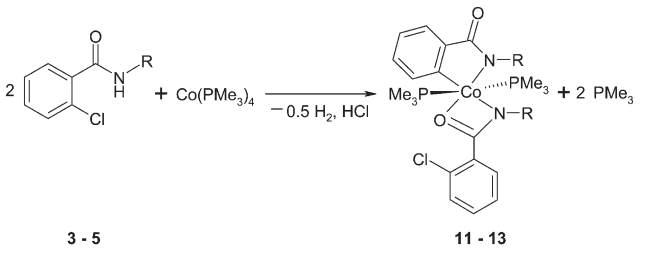
2 **10** (2)

With the carbonyl-O atom as an anchoring group, the oxidative addition reaction of the C–Cl bond on the cobalt(0) center proceeds. Product **10** is a penta-coordinate cation with the cobalt (II) center and the counter-ion is the chlorine anion. In the infrared spectrum of complex **10** the characteristic ν(C═O) band is found at 1595 cm^{-1} showing a bathochromic shift by 67 cm^{-1} comparing with that of the free ligand, while the typical vibration of a PMe_3 ligand is recorded at 940 cm^{-1}. The ν(N–H) band is changed from 3304 cm^{-1} for benzamide **2** to 3230 cm^{-1} for complex **10** owing to the coordination of the C═O to the Co atom and the weakening of the N–H band.

The molecular structure of complex **10** (Fig. 4) confirms a distorted square-pyramidal coordination of the cobalt(II) center with an O atom in the apical position and three PMe_3 groups as well as a phenyl-C atom in the equatorial plane. The P1–Co–P2 angle is 166.54°. This is equal to the angle C1–Co–P3. The long distance of 2.8182(10) Å between Co and the Cl atom in complex **10** indicates that no covalent interaction between the cobalt and chlorine atoms exists because the average Co(II)–Cl length is much shorter.[13] The chloride ion is located as a counter-ion outside the chelate cobalt cation. The bite angle C1–Co–O1 of 80.27(10)° is in the normal region. The sum (362.0°) of the four angles [C1–Co–P1 = 84.31(10), C1–Co–P2 = 86.62(10), P1–Co–P3 = 95.78(4) and P2–Co–P3 95.36(4)°] around the central cobalt atom proves that the co-planarity of the five atoms [CoC1P1P2P3] is poor. The five-membered chelate ring and the phenyl ring are in one plane. The butyl group is almost perpendicular to this plane due to the packing effect in the crystal cell.

Under similar reaction conditions the reaction of $Co(PMe_3)_4$ with the *ortho*-chlorinated benzamides **3–5** (R = Ph (**3**); (4-Me)Ph (**4**) and (4-Cl)Ph (**5**)) containing a phenyl group on the N atom did not afford the analogous complexes to penta-coordinate Co(II) complex **10**, but hexa-coordinate bis-chelate cobalt(III) complexes **11–13** were obtained *via* the C–Cl bond cleavage of one benzamide molecule (eqn (3)). The deprotonation of the (NH)-group of the second benzamide supports this transformation with the escape of HCl. This benzamide coordinates to the cobalt atom with [*N*, *O*]-coordination to form a four-membered chelate ring. The five-membered chelate ring with [*C*, *N*]-coordination is formed through C–Cl bond activation and N–H bond cleavage.

The IR spectra of cobalt(III) complexes **11–13** clearly indicates the disappearance of the N–H bond. This shows us that both of the NH-groups of the amides are deprotonated in the reaction. In the ^{31}P NMR spectra two phosphorus nuclei resonate at 4.3 ppm



(3)

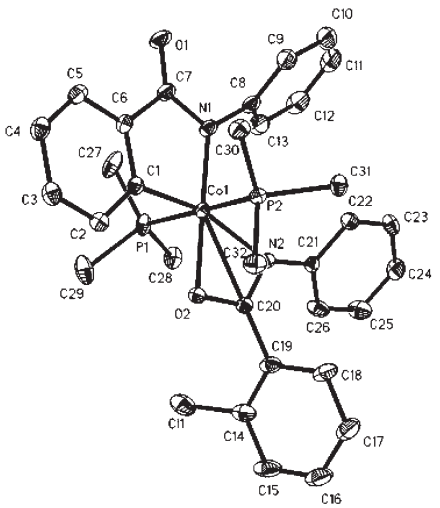


Fig. 5 Molecular structure of **11** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): Co1–C1 1.902(2), Co1–N1 1.9410(17), Co1–O2 1.9712(14), Co1–N2 2.1187(18), Co1–P1 2.2449(7), Co1–P2 2.2540(6), C1–Co1–N1 83.52(8), N1–Co1–O2 179.13(7), C1–Co1–P1 89.02(6), N1–Co1–P1 92.73(6), O2–Co1–P1 87.36(5), N2–Co1–P1 93.01(5), C1–Co1–P2 84.52(6), N1–Co1–P2 89.59(6), O2–Co1–P2 90.41(5), N2–Co1–P2 92.18(5), P1–Co1–P2 172.84(2).

in complex **11**, at 4.5 ppm in complex **12** and at 5.2 ppm in complex **13** as a singlet. This illustrates that two PMe_3 ligands have the same chemical environment in the solution.

The molecular structures of complexes **11** and **12** (Fig. 5 and 6) confirm the hexa-coordinate octahedral geometry of these two complexes. In the molecular structure of complex **11** a five-membered metallacycle [C1C6C7N1Co1] is formed through the coordination of the N1 atom of the amide group and the *ortho*-metalated phenyl-C1 atom, while a four-membered chelate ring [N2C20O2Co1] is formed with the amide as an anion ligand through deprotonation of the NH group. Both the five-membered and the four-membered chelate rings are coplanar. Two trimethylphosphine ligands are in the axial position with the angle of P1–Co1–P2 of 172.84(2)°. The bite angle (N2–Co1–O2 = 64.67(7)°) of the four-membered chelate ring is much smaller than that (C1–Co–N1 = 83.52(8)°) of the five-membered chelate ring, as expected. Because of the repulsion and the packing

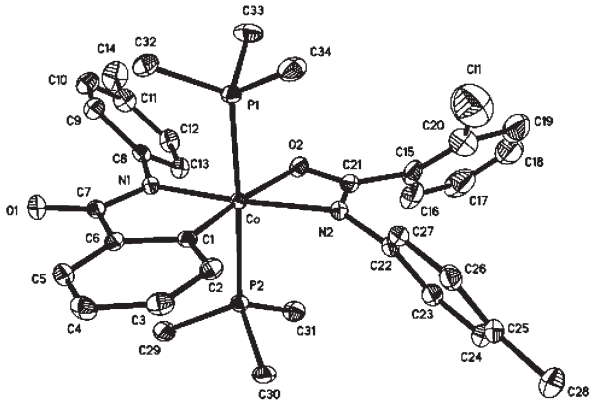
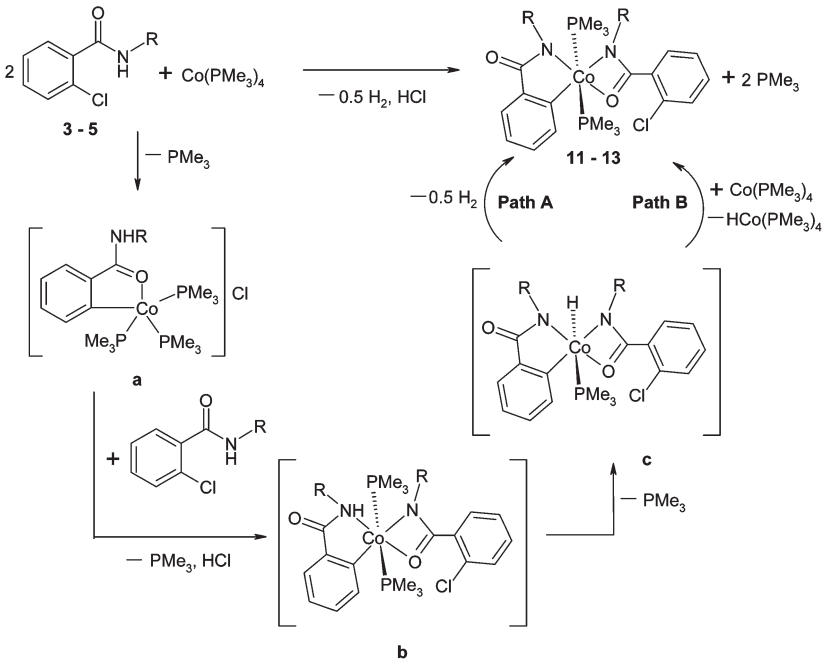


Fig. 6 Molecular structure of **12** (all hydrogen atoms were omitted for clarity). Selected distances (Å) and angles (°): Co–N1 1.953(4), Co–N2 2.021(4), Co–O2 2.055(3), Co–P1 2.2430(13), Co–P2 2.2489(12) C1–Co–N1 83.64(17), N1–Co–N2 168.41(16), N1–Co–O2 103.65(14), C1–Co–P1 90.58(13), N1–Co–P1 86.54(11), N2–Co–P1 94.11(11), O2–Co–P1 89.93(10), C1–Co–P2 86.43(13), N1–Co–P2 91.41(11), N2–Co–P2 88.45(11), N2–Co–O2 64.80(14), O2–Co–P2 93.25(10), P1–Co–P2 176.55(5).

effect the three phenyl groups, phenyl-[C8-C13], phenyl-[C14-C19] and phenyl-[C21-C26] are neither in the equatorial plane nor in the same plane. They have different dihedral angles among them. The sum of the angles around the two N-atoms are 360° [for N1 atom: C7–N1–C8 (118.4(2)°) + C7–N1–Co1 (116.16(16)°) + C8–N1–Co1 (125.46(16)°) = 360.02°; for N2 atom: C20–N2–C21 (123.30(19)°) + C20–N2–Co1 (86.63(14)°) + C21–N2–Co1 (150.01(15)°) = 359.94°], which indicates that both N atoms nearly have planar configuration. The sp^3-hybrid state of the N atom in the "free" benzamides changed to the sp^2-hybrid state of the N atom in the cobalt(III) complexes. This transformation is supported by the phenyl group on the N atom because of the "large" π-conjugation.

The molecular structure of complex **12** is similar to that of **11**, the only difference is that two N-atoms are *trans*-situated in complex **12**, while the two N-atoms in complex **11** are *cis*-orientated. The reason of this difference is not unclear. Owing to the strong *trans*-effect of the coordinated phenyl-C atom, Co–N2 bond distance (Co1–N2 = 2.1187(18) Å) in complex **11** is considerably longer than that (Co–N2 = 2.021(4) Å) in complex **12**, while the Co–O2 bond distance (Co–O2 = 2.055(3) Å) in complex **12** is also longer than that (Co1–O2 = 1.9712 Å) in complex **11** for the same reason.

The formation mechanism of complexes **11–13** is suggested in Scheme 1. The first step is C–Cl bond cleavage to form a cobalt(II) cation intermediate **a**, as complex **10**. This process is supported and compensated through cyclometalation with an O-atom as an anchoring group. The deprotonation of the NH-group of the second benzamide molecule affords the intermediate **b** with the escape of HCl. The N–H bond activation of the coordinated benzamide generates the hydrido intermediate **c**. Intermolecular elimination of H_2 delivers the end products **11–13** (path A). The alternative route from intermediate **c** to end products **11–13** is path B. The reaction of intermediate **c** with $Co(PMe_3)_4$ gives rise to end products **11–13** with the formation of $HCo(PMe_3)_4$, but $HCo(PMe_3)_4$ was not observed by *in situ* IR. The precipitation of the trimethylphosphonium chloride,

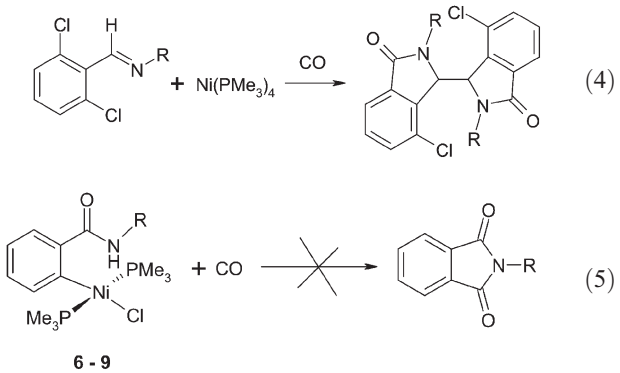


Scheme 1

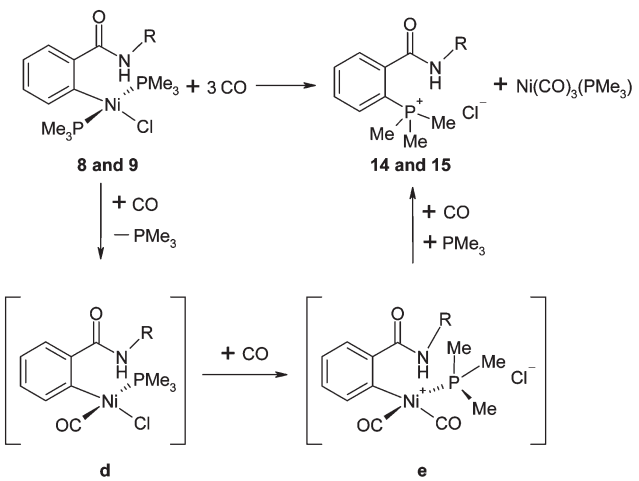
[Me_3PH]Cl, from the mother solution is an evidence of the formation of HCl. In these three reactions the deprotonation of the amide-NH group is possibly supported by the phenyl (**11**) or the phenyl derivatives (aromatic group) on the N-atom (**12** and **13**) because the deprotonated amide is a "larger" conjugated system with the anion [NCO]-moiety containing two phenyl groups, one attached to the carbon atom and the other linked to the nitrogen atom. For this reason no deprotonation product of the NH-group was found with the butyl group (aliphatic) on the amide-N atom in eqn (2).

3.3. Reaction of complexes 6–9 with CO

In 2008 we synthesized a series of bis(isoindolinone) through carbonylative cyclization and dimerization of phenylimine with $Ni(PMe_3)_4$ stoichiometric amounts *via* C–Cl bond activation under a CO atmosphere at room temperature (eqn (4)).[10] Under the same conditions, metal amide complexes **6–9** could not transform to heterocyclic compounds 2-alkylisoindoline-1,3-dione *via* cyclization as expected (eqn (5)).

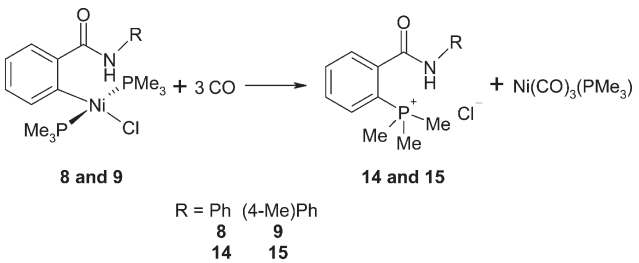


Complexes **8** and **9** as starting materials under 1 bar of CO at room temperature unexpectedly converted to phosphonium salts



Scheme 2

14 and **15** (eqn (6)). The byproduct $Ni(CO)_3(PMe_3)$ was confirmed by IR.[14]



The proposed mechanism of the formation of phosphonium salts **14** and **15** is shown in Scheme 2. The ligand replacement of trimethylphosphine by carbon monoxide in complexes **8** and

9 to form the mono-carbonyl intermediate **d** is the first step. The further carbonylation of the intermediate **d** gives rise to the intermediate **e** with the dissociation of the chlorine ligand and the formation of the positively-charged nickel center. The unstable intermediate **e** transforms to the end products **14** and **15** *via* reductive elimination and quaternization of trimethyphosphine with the formation of $Ni(CO)_3(PMe_3)$.

The phosphonium salt, as a Lewis acid, can be used in organocatalysis. The most prominent catalytic application of this kind of compound is as a phase-transfer catalyst.[15] Several related catalytic systems were developed using phosphonium salts as catalysts.[16–19]

4. Conclusion

In summary the C–Cl bonds of *ortho*-chlorinated benzamides **1–5** were successfully activated by tetrakis(trimethylphosphine)-nickel(0) and tetrakis(trimethylphosphine)cobalt(0). The *trans*-four-coordinate nickel(II) chloride complexes **6–9**, as C–Cl bond activation products, were obtained without coordination of the amide groups. In the case of benzamide **2**, ionic cobalt(II) chloride **10**, as a C–Cl bond activation product, was isolated. If, instead of the *n*-butyl group on the amide-N atom (as in **2**), the substituent on the amide-N atom is phenyl or its derivatives (as in **3–5**), the hexa-coordinate bis-chelate cobalt(III) complexes **11–13** could be obtained *via* the reaction of the amides **3–5** with $[Co(PMe_3)_4]$. The phosphonium salts **14** and **15** were obtained by reaction of complexes **3** and **4**, respectively, as a starting material under 1 bar of CO at room temperature. The crystal and molecular structures of complexes **6**, **7**, **9**, **10**, **11** and **12** were determined by single-crystal X-ray diffraction.

Acknowledgements

We gratefully acknowledge the supports by NSF China No. 20872080 and from Prof. Dr. Dieter Fenske (Karlsruhe Nano-Micro Facility, KNMF).

Notes and references

1 (*a*) O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCBs*, CRC Press, Cleveland, OH, 1974; (*b*) P. J. Squillace, M. J. Moran, W. W. Lapham, C. V. Price, R. M. Clawges and J. S. Zogorski, *Environ. Sci. Technol.*, 1999, **33**, 4176; (*c*) R. E. Doherty, *Environ. Forensics*, 2000, **1**, 69.

2 (*a*) V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047; (*b*) M. Cucullu, S. P. Nolan, T. R. Belderrain and R. H. Grubbs, *Organometallics*, 1999, **18**, 1299; (*c*) M. Portnoy and D. Mieltein, *Organometallics*, 1993, **12**, 1665; (*d*) K. Ferre, G. Poignant, L. Toupet and V. Guerchais, *J. Organomet. Chem.*, 2001, **629**, 19; (*e*) A. Aballay, F. Godoy, G. E. Buono-Core, A. H. Klahn, B. Oelckers, M. T. Garland and J. C. Munoz, *J. Organomet. Chem.*, 2003, **688**, 168; (*f*) D. Donnecke, K. Halbauer and W. Imhof, *J. Organomet. Chem.*, 2004, **689**, 2707.

3 (*a*) T. Yamamoto, M. Nishiyama and Y. Koie, *Tetrahedron Lett.*, 1998, **39**, 2367; (*b*) M. Kawatsura and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 1473; (*c*) M. W. Hooper, M. Utsunomiya and J. F. Hartwig, *J. Org. Chem.*, 2003, **68**, 2861; (*d*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 1998, **37**, 3387; (*e*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 1999, **38**, 2411; (*f*) A. F. Littke, C. Dai and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020; (*g*) A. Aranyos, D. W. Old, A. Kiyomori, J. P. Wolfe, J. P. Sadighi and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 4369; (*h*) J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550; (*i*) J. Yin, M. P. Rainka, X.-X. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 1162; (*j*) X. Huang, K. W. Anderson, D. Zim, L. Jiang, A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2003, **125**, 6653; (*k*) S. D. Walker, T. E. Barder, J. R. Martinelli and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2004, **43**, 1871; (*l*) C. W. K. Gstöttmayr, V. P. W. Bohm, E. Herdtweck, M. Grosche and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1363.

4 (*a*) C. Chen and L.-M. Yang, *Tetrahedron Lett.*, 2007, **48**, 2427; (*b*) J.-C. Galland, M. Savignac and J.-P. Genêt, *Tetrahedron Lett.*, 1999, **40**, 2323; (*c*) A. F. Indolese, *Tetrahedron Lett.*, 1997, **38**, 3513; (*d*) S. Saito, S. Ohtani and N. Miyaura, *J. Org. Chem.*, 1997, **62**, 8024; (*e*) F. Mongin, L. Mojovic, B. Guillamet, F. Trecourt and G. Que'guiner, *J. Org. Chem.*, 2002, **67**, 8991; (*f*) A. Steffen, M. I. Sladek, T. Braun, B. Neumann and H.-G. Stammler, *Organometallics*, 2005, **24**, 4057; (*g*) Y. Ohnishi, Y. Nakao, H. Sato, T. Hiyama and S. Sakaki, *Organometallics*, 2009, **28**, 2583.

5 (*a*) For an excellent review see: H. Shinokubo and K. Oshima, *Eur. J. Org. Chem.*, 2004, 2081; (*b*) T. Fujioka, T. Nakamura, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2002, **4**, 2257; (*c*) T. Tsuji, H. Yorimitsu and K. Oshima, *Angew. Chem., Int. Ed.*, 2002, **41**, 4137; (*d*) K. Wakabayashi, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2001, **123**, 5374; (*e*) H. Ohmiya, T. Tsuji, H. Yorimitsu and K. Oshima, *Chem.–Eur. J.*, 2004, **10**, 5640; (*f*) Y. Ikeda, T. Nakamura, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2002, **124**, 6514; (*g*) K. Mizutani, H. Shinokubo and K. Oshima, *Org. Lett.*, 2003, **5**, 3959; (*h*) P. Gomes, C. Gosmini and J. Prichon, *Org. Lett.*, 2003, **5**, 1043; (*i*) P. Gomes, C. Gosmini and J. Prichon, *Synthesis*, 2003, 1909; (*j*) C. K. Reddy and P. Knochel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1700; (*k*) T. J. Korn, G. Cahiez and P. Knochel, *Synlett*, 2003, 1892; (*l*) T. J. Korn, G. Cahiez and P. Knochel, *Angew. Chem., Int. Ed.*, 2005, **44**, 2947.

6 (*a*) V. V. Grushin and W. J. Marshall, *J. Am. Chem. Soc.*, 2004, **126**, 3068; (*b*) S. A. Macgregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov and V. V. Grushin, *J. Am. Chem. Soc.*, 2005, **127**, 15304.

7 (*a*) Q. Chen and C. Li, *Organometallics*, 2007, **26**, 223; (*b*) H. Guo, K. Kanno and T. Takahashi, *Chem. Lett.*, 2004, **33**, 1356; (*c*) L. K. Ottesen, F. Ek and R. Olsson, *Org. Lett.*, 2006, **8**, 1771; (*d*) A. Fürstner, A. Leitner, M. Me'ndez and H. Krause, *J. Am. Chem. Soc.*, 2002, **124**, 13856; (*e*) A. Fürstner and A. Leitner, *Angew. Chem., Int. Ed.*, 2002, **41**, 609; (*f*) D. Donnecke, K. Halbauer and W. J. Imhof, *J. Organomet. Chem.*, 2004, **689**, 2707; (*g*) W. Imhof and A. Gobel, *J. Organomet. Chem.*, 2000, **610**, 102.

8 Y. Chen, H. Sun, U. Flörke and X. Li, *Organometallics*, 2008, **27**, 271.

9 Y. Shi, M. Li, Q. Hu, X. Li and H. Sun, *Organometallics*, 2009, **28**, 2209.

10 R. Cao, H. Sun and X. Li, *Organometallics*, 2008, **27**, 1944.

11 (*a*) H.-F. Klein and H. H. Karsch, *Angew. Chem.*, 1970, **82**, 885; (*b*) H.-F. Klein and H. H. Karsch, *Chem. Ber.*, 1975, **108**, 944.

12 (*a*) H. Y. Kwon, S. Y. Lee, B. Y. Lee, D. M. Shin and Y. K. Chung, *Dalton Trans.*, 2004, 921–928; (*b*) N. V. Kaminskaia, G. M. Ullmann, D. B. Fulton and N. M. Kostic, *Inorg. Chem.*, 2000, **39**, 5004; (*c*) Y. N. Belokon, N. B. Bespalova, T. D. Churkina, I. Císařová, M. G. Ezernitskaya, S. R. Harutyunyan and R. Hrdina, *J. Am. Chem. Soc.*, 2003, **125**, 12860; (*d*) B. Y. Lee, G. C. Bazan, J. Vela, Z. G. A. Komon and X. Bu, *J. Am. Chem. Soc.*, 2001, **123**, 5352.

13 (*a*) A. H. Klahn, A. Toro, B. Oelckers, V. Manriquez and O. Wittke, *Organometallics*, 2000, **19**, 2580; (*b*) A. Steffen, M. I. Sladek, T. Breun, B. Neumann and H.-G. Stammler, *Organometallics*, 2005, **24**, 4057; (*c*) J. Ito, T. Miyakawa and H. Nishiyama, *Organometallics*, 2008, **27**, 3312.

14 C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956.

15 T. Werner, *Adv. Synth. Catal.*, 2009, **351**, 1469.

16 M. Kohler, PhD Thesis, RWTH Aachen, Germany, 2003.

17 A. Bohsako, C. Asakura and T. Shioiri, *Synlett*, 1995, 1033.

18 J. McNulty, V. Dyck, A. Larichev, A. Capretta and J. Robertson, *Lett. Org. Chem.*, 2004, **1**, 137.

19 T. Akiyama, Y. Tamura, J. Itoh, H. Morita and K. Fuchibe, *Synlett*, 2006, 141.

