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Oxidation–reduction exchange of 2-acylenolato and trimethylphosphane ligands between d^6 and d^8 complexes of nickel and cobalt

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Dedicated to H. Schmidbaur on the occasion of his 65th birthday

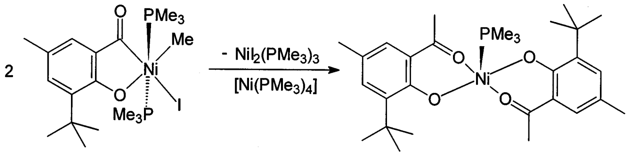
Abstract

A series of five (C:O)-dianionic 1-acyl-2-enolato ligands C(O)–C=C–O in a transmetallation reaction between 18-electron metal-d^6 complexes *mer-trans*-NiMe(X)[C(O)–C=C–O]$(PMe_3)_2$ [C=C=C_6H_4, X = I (**1**); C=C=3-CMe_3-5-Me-C_6H_2, X = I (**2**); C=C=5,6-benzo-C_6H_2, X = I (**3**); C=C=3,4-benzo-cyclohexene, X = Br (**4**); C=C=1,2-diphenylethene, X = I (**5**)] and the 18-electron metal-d^8 compound $CoMe(PMe_3)_4$ (1:2), undergo a reductive coupling of acyl and methylnickel functions involving the C(O)–C=C–O ligands. Subsequent migration of methyl groups between cobalt intermediates generates three products: *mer-trans*-$CoMe_2$[MeC(O)–C=C–O]$(PMe_3)_2$ (**6**–**10**), $Ni(PMe_3)_4$, and $CoX(PMe_3)_3$. The X-ray crystal structure of compound **7** has been determined. The methyl ligands are found in positions opposite to the O-donor functions. Upon replacing the aromatic rings in salicylaldehyde derivatives C(O)–C=C–O by more flexible cyclohexene rings or acyclic systems the reduction of Ni(IV) complexes follows a different course. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxidation/reduction; Cobalt complexes; Nickel complexes; 2-Acylenolato complexes; Transmetallation reaction

1. Introduction

Octahedral methyl(acylphenolato)nickel(IV) halide complexes in the presence of $Ni(PMe_3)_4$ as a catalyst undergo a reductive C,C-coupling reaction [1] according to Eq. (1). In a subsequent ligand dismutation reaction two of the resulting 2-acetylphenolate ions become coordinated as bidentate ligands to the same nickel centre.



(1)

We have been looking for low-valent trimethylphosphine complexes of cobalt that would similarly act as one-electron reductants and serve as catalysts for the C,C-coupling. In terms of reductive power, $CoMe(PMe_3)_4$ would be close to $Ni(PMe_3)_4$. However, due to the presence of the methyl function a catalytic cycle is difficult to close. In stoichiometric reactions an exchange of 2-acetylphenolate ions is then envisaged to occur between the two metals.

When reacting nickel (d^6) with cobalt (d^8) compounds, we discovered a new type of bidentate ligand transfer which proceeds as an inequivalent exchange process [2] and effects a transmetallation reaction by multistep oxidation/reduction processes.

If odd-electron species are ruled out, an inequivalent exchange of chelating acylenolato ligands and trimethylphosphines between d^8 complexes of nickel and cobalt can be described by oxidation/reduction

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reactions of the metals according to the schematic Eq. (a).

$$\text{dianionic: Ni }(d^8) + \text{Co }(d^8) = \text{Co }(d^6) + \text{Ni }(d^{10}) \quad \text{(a)}$$

$$\text{CNiC }(d^6) = \text{Ni }(d^8) + \text{CC} \quad \text{(b)}$$

$$\text{monoanionic: Ni }(d^8) + 2\text{Co }(d^8) = \text{Co }(d^6) + \text{Ni }(d^{10}) + \text{Co }(d^8) \quad \text{(c)}$$

When combined with the reductive coupling (Eq. (b)) an inequivalent exchange of monoanions requires a 1:2 stoichiometry (Eq. (c)) because a total of four anionic functions have to be accommodated in the products: 2-acetylphenolate, halide and two methyl groups. Prediction of preferential coordination would place an O:O-coordinated 2-acetylphenolato ligand at a Co (d^6) site but would not be strict for the remaining groups. Experiments were designed in order to test this prediction and to learn more about preferential coordination of trimethylphosphine and chelating monoanionic and dianionic ligands containing hard and soft donor atoms in metal coordination numbers five and six.

2. Experimental

2.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Details of characterisation and spectroscopic instrumentation have been given elsewhere [3].

2-Formyl-4-phenyl-cyclohexanone, 2-formyl-4-*tert*-butyl-cyclohexanone, and 3-hydroxy-2,3-diphenyl-propenal were obtained by literature methods [4]. (2-Oxobenzoyl)tris(trimethylphosphine)nickel [5], (2-oxonaphthoyl)tris(trimethylphosphine)nickel [5], [(1,2-diphenyl-2-oxoethene-1-yl)carbonyl]tris(trimethylphosphine)nickel [2], $Co(CCPh)(PMe_3)_4$ [6], $CoMe(PMe_3)_4$ [6], $Co(PMe_3)_4$ [6], *mer*-$CoMe_3(PMe_3)_3$ [7], (3-carbonyl-4-oxo-1,2-dihydro-naphthalenyl)tris(trimethylphosphine)nickel [2], [(5-*tert*-butyl-2-oxocyclohexen-1-yl) carbonyl]tris(trimethylphosphine)nickel [2], and the methylnickel(IV) complexes **2** [1] and **11** [2] were prepared by published procedures. Other chemicals (Aldrich) were used as purchased.

2.2. Procedures

2.2.1. Synthesis of mer-trans-iodo(methyl)-(2-oxobenzoyl)bis(trimethylphosphine)nickel (1)

A sample containing 1110 mg of (2-oxobenzoyl)-tris(trimethylphosphine)nickel (1.70 mmol) and 842 mg of iodomethane (5.94 mmol) in 40 ml of acetonitrile at 0°C turned dark brown within 20 min, depositing first a white and finally a yellow solid. The solids were isolated by filtration and washed with ether. Extraction with 60 ml of THF over a glass-sinter disc (G4) and evaporation of the solvent yielded a light yellow powder (460 mg, 36%), dec. > 230°C.

Anal. Calc. for $C_{14}H_{25}INiO_2P_2$ (472.8): C, 35.35; H, 5.33. Found: C, 34.73; H, 5.25%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1725vs. ^1H NMR (200 MHz, THF-d_8, 296 K): δ 1.25 (t, $^3J(PH) = 7.9$ Hz, 3H, NiCH_3), 1.49 (t′, $|^2J(PH) + {}^4J(PH)| = 7.7$ Hz, 18H, PCH_3), 6.35 (t, $^3J(HH) = 7.3$ Hz, 1H, CH), 7.2 (m, 2H, CH), 7.76 (d, $^3J(HH) = 8.6$ Hz, 1H, CH). $^{31}P\{^1H\}$ NMR (81.0 MHz, THF-d_8, 296 K): δ 14.3 (s).

2.2.2. Synthesis of mer-trans-iodo(methyl)-(2-oxo-1-naphthoyl)bis(trimethylphosphine)nickel (3)

A sample containing 820 mg of (2-oxonaphthoyl)-tris(trimethylphosphine)nickel (1.79 mmol) and 560 mg of iodomethane (3.94 mmol) in 40 ml of acetonitrile at −30°C turned olive–green within 20 min, depositing first a white and finally a yellow solid. After 40 min workup as for **1** a yellow powder was obtained (480 mg, 51%), dec. > 250°C.

Anal. Calc. for $C_{18}H_{27}INiO_2P_2$ (522.8): C, 41.32; H, 5.20. Found: C, 41.58; H, 5.24%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1697vs. ^1H NMR (200 MHz, THF-d_8, 296 K): δ 1.26 (t, $^3J(PH) = 8.0$ Hz, 3H, NiCH_3), 1.48 (t′, $|^2J(PH) + {}^4J(PH)| = 8.4$ Hz, 18H, PCH_3), 6.96 (d, $^3J(HH) = 9.2$ Hz, 1H, CH), 7.16 (t, $^3J(HH) = 7.6$ Hz, 1H, CH), 7.43 (t, $^3J(HH) = 7.6$ Hz, 1H, CH), 7.6 (m, 2H, CH), 8.33 (d, $^3J(HH) = 8.3$ Hz, 1H, CH). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 296 K): δ 13.6 (t′, $|^1J(PC) + {}^3J(PC)| = 33.4$ Hz, PCH_3), 27.1 (C(O)CH_3), 122.4, 122.9, 128.2, 129.4, 137.8 (CH). $^{31}P\{^1H\}$ NMR (81 MHz, THF-d_8, 296 K): δ 14.5 (s).

2.2.3. Synthesis of mer-trans-bromo(methyl)-(3-carbonyl-4-oxo-1,2-dihydronaphthalenyl)-bis(trimethylphosphine)nickel (4)

A sample containing 6.04 g of (3-carbonyl-4-oxo-1,2-dihydronaphthalenyl)tris(trimethylphosphine)nickel (13.2 mmol) and 3.7 g of bromomethane (39.0 mmol) in 50 ml of acetonitrile at −30°C turned red–brown within 15 min, depositing first a white and finally a yellow solid. Washing with 20 ml of cold ether followed by 30 ml of water left a yellow solid which was recrystallised from ether (4.50 g, 71%), dec. > 104°C.

Anal. Calc. for $C_{18}H_{29}BrNiO_2P_2$ (478.0): C, 45.23; H, 6.12. Found: C, 45.01; H, 6.57%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1686vs. ^1H NMR (300 MHz, THF-d_8, 243 K): δ 1.10 (t, $^3J(PH) = 8.3$ Hz, 3H, NiCH_3), 1.43 (t′, $|^2J(PH) + {}^4J(PH)| = 8.3$ Hz, 18H, PCH_3), 2.48 (t, $^3J(HH) = 7.3$ Hz, 2H, CH_2), 2.82 (m, 2H, CH_2), 7.3 (m, 3H, CH_2), 7.88 (d, $^3J(HH) = 6.5$ Hz, 1H, CH).

2.2.4. *Synthesis of mer-trans-iodo(methyl)-(1-carbonyl-2-oxo-1,2-diphenyl-diyl)-bis(trimethylphosphine)nickel (**5**)*

A sample containing 4.40 g of [(1,2-diphenyl-2-oxo-ethene-1-yl)carbonyl]tris(trimethylphosphine)nickel (8.64 mmol) and 3.50 g of iodomethane (24.7 mmol) in 40 ml of acetonitrile at -30°C turned brown within 15 min, depositing first a white and finally a yellow solid. Workup as with **4** produced a yellow powder (4.36 g, 88%), dec. >101°C.

Anal. Calc. for $C_{22}H_{31}INiO_2P_2$ (575.0): C, 45.95; H, 5.43. Found: C, 45.52; H, 6.10%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1696vs, 1678m. ^{1}H NMR (200 MHz, THF-d$_8$, 296 K): δ 1.15 (t, $^3J(\mathrm{PH}) = 8.2$ Hz, 3H, NiCH_3), 1.60 (t′, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})| = 8.3$ Hz, 18H, PCH_3), 7.20 (m, 10H, CH).

2.2.5. *Synthesis of (2-acetylphenolato-O:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt (**6**)*

Method a: A total of 930 mg **1** (1.97 mmol) and 1520 mg $CoMe(PMe_3)_4$ (4.03 mmol) in 60 ml of ether formed a red–brown mixture within 20 h at 20°C, from which a blue solid of $CoI(PMe_3)_3$ (IR) was removed by filtration. The filtrate was taken to dryness in vacuo, and the brown residue was extracted with pentane to afford bunches of red needles (200 mg, 27%).

Method b: A sample containing 800 mg of 2-acetylphenol (5.88 mmol) and 1430 mg of *mer*-$CoMe_3(PMe_3)_3$ (4.31 mmol) in 40 ml of ether at 20°C, formed a red solution which turned brown, within 1 h, under slow evolution of gas. After 2 h the mixture was filtered and the filtrate was kept at -27°C to yield red platelets which were dried in vacuo (1090 mg, 62%), dec. >135°C.

Anal. Calc. for $C_{16}H_{31}CoO_2P_2$ (376.3): C, 51.07; H, 8.30; P, 16.46. Found: C, 51.11; H, 8.26; P, 16.63%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1611s, 1588s. ^{1}H NMR (200 MHz, THF-d$_8$, 296 K): δ -0.77 (t, $^3J(\mathrm{PH}) = 8.9$ Hz, 3H, CoCH_3), -0.61 (t, $^3J(\mathrm{PH}) = 9.5$ Hz, 3H, CoCH_3), 1.12 (t′, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})| = 6.5$ Hz, 18H, PCH_3), 1.73 (s, 3H, C(O)CH_3), 6.0–7.3 (m, 4H, CH). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d$_8$, 297 K): δ -16.6 (s, br, CoCH$_3$), 10.8 (t′, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 20.3$ Hz, PCH$_3$), 27.1 (C(O)CH$_3$), 111.3, 127.9, 132.9, 135.2 (CH), 121.4 (CC(O)CH$_3$), 174.5 (CO), 197.5 (C(O)CH$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d$_8$, 297 K): δ 14.6 (s, br).

2.2.6. *Synthesis of (2-acetyl-4-methyl-6-tert-butylphenolato-O:O)-cis-dimethyl-trans-bis-(trimethylphosphine)cobalt (**7**)*

A sample containing 2480 mg of **2** (4.67 mmol) and 3460 mg of $CoMe(PMe_3)_4$ (9.16 mmol) in 80 ml of ether formed a red–brown mixture, within 20 h at 20°C. Workup as above (method a) afforded red–brown platelets (1320 mg, 65%), dec. >151°C.

Anal. Calc. for $C_{21}H_{41}CoO_2P_2$ (446.4): C, 56.50; H, 9.26; P, 13.88. Found: C, 56.68; H, 8.91; P, 13.71%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1619w, 1580s. ^{1}H NMR (200 MHz, THF-d$_8$, 296 K): δ -0.81 (t, $^3J(\mathrm{PH}) = 9.2$ Hz, 3H, CoCH_3), -0.47 (t, $^3J(\mathrm{PH}) = 9.0$ Hz, 3H, CoCH_3), 1.12 (s, 18H, PCH_3), 1.26 (s, 9H, C(CH_3)$_3$), 2.05 (s, 3H, CCH_3), 2.24 (s, 3H, C(O)CH_3), 6.9–7.0 (m, 2H, CH). ^{13}C{^{1}H} NMR (50.3 MHz, THF-d$_8$, 296 K): δ -15.4 (s, br, CoCH$_3$), 11.6 (t′, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 20.2$ Hz, PCH$_3$), 20.9 (CCH$_3$), 28.2 (C(O)CH$_3$), 30.6 (C(CH$_3$)$_3$), 35.6 (C(CH$_3$)$_3$), 120.8, 134.0, 144.8 (C), 118.2, 130.0 (CH), 173.1 (CO), 197.3 (C(O)CH$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d$_8$, 233 K): δ 19.7 (s, br).

2.2.7. *Synthesis of (1-acetyl-2-naphtholato-O:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt (**8**)*

A sample containing 1000 mg of **3** (1.91 mmol) and 1450 mg of $CoMe(PMe_3)_4$ (3.84 mmol) in 50 ml of ether slowly formed a red–brown mixture. After 18 h at 20°C workup as above (method a) afforded bunches of dark red needles (550 mg, 67%), dec. >123°C.

Anal. Calc. for $C_{20}H_{33}CoO_2P_2$ (426.4): C, 56.34; H, 7.80. Found: C, 56.02; H, 8.11%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1614s, 1577s. ^{1}H NMR (300 MHz, THF-d$_8$, 297 K): δ -0.72 (t, $^3J(\mathrm{PH}) = 9.5$ Hz, 3H, CoCH_3), -0.66 (t, $^3J(\mathrm{PH}) = 9.5$ Hz, 3H, CoCH_3), 1.13 (s, 18H, PCH_3), 2.36 (s, 3H, C(O)CH_3), 6.6–7.1 (m, 6H, CH). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d$_8$, 297 K): δ 10.9 (t′, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 21.0$ Hz, PCH$_3$), 31.0 (C(O)CH$_3$), 117.3 (CC(O)CH$_3$), 121.8, 125.3, 127.2, 128.9, 129.5, 135.1 (CH), 127.7, 136.6 (C), 177.3 (CO), 193.9 (C(O)CH$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, THF-d$_8$, 233 K): δ 20.6 (s, br).

2.2.8. *Synthesis of (3-acetyl-4-oxo-1,2-dihydronaphthalenyl-O:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt (**9**)*

A sample containing 940 mg of **4** (1.97 mmol) and 1520 mg of $CoMe(PMe_3)_4$ (4.02 mmol) in 50 ml of ether formed a red–brown mixture, within 18 h at 20°C. Workup as above (method a) afforded (besides a blue solid of $CoBr(PMe_3)_3$ [8], IR) bunches of dark red crystals (470 mg, 56%), dec. >145°C.

Anal. Calc. for $C_{20}H_{35}CoO_2P_2$ (428.4): C, 56.08; H, 8.23. Found: C, 55.67; H, 8.40%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1606s, 1584s. ^{1}H NMR (200 MHz, THF-d$_8$, 296 K): δ -0.68 (t, $^3J(\mathrm{PH}) = 9.4$ Hz, 3H, CoCH_3), -0.64 (t, $^3J(\mathrm{PH}) = 9.4$ Hz, 3H, CoCH_3), 1.36 (t′, $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})| = 5.8$ Hz, 18H, PCH_3), 1.91 (s, 3H, C(O)CH_3), 2.50 (m, 2H, CH_2), 2.70 (m, 2H, CH_2), 7.4–7.8 (m, 4H, CH). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d$_8$, 296 K): δ 10.8 (t′, $|^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})| = 20.0$ Hz, PCH$_3$), 26.8 (C(O)CH$_3$), 26.1, 30.1 (CH_2), 104.2 ($CC(O)CH_3$), 126.8, 126.9, 127.3, 129.8 (CH), 137.2, 140.5 (C), 176.1 (CO), 187.8 ($C(O)CH_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, 296 K): δ 13.6 (s, br).

*2.2.9. Synthesis of (1-acetyl-2-oxo-1,2-diphenyl-diyl-O:O)-cis-dimethyl-trans-bis(trimethyl-phosphine)-cobalt (**10**)*

A sample containing 1030 mg of **5** (1.79 mmol) and 1350 mg of $CoMe(PMe_3)_4$ (3.58 mmol) in 60 ml of ether at 20°C formed a dark brown mixture, within 18 h. Workup as above (method a) afforded red–brown needles (600 mg, 70%), dec. >142°C.

Anal. Calc. for $C_{24}H_{37}CoO_2P_2$ (478.4): C, 60.25; H, 7.79. Found: C, 60.41; H, 8.03%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1582m, 1561m. ^1H NMR (300 MHz, acetone-d_6, 297 K): δ -0.67 (t, $^3J(PH) = 9.5$ Hz, 3H, $CoCH_3$), -0.65 (t, $^3J(PH) = 9.5$ Hz, 3H, $CoCH_3$), 1.27 (t′, $|^2J(PH) + {}^4J(PH)| = 9.2$ Hz, 18H, PCH_3), 1.63 (s, 3H, $C(O)CH_3$), 7.0–7.1 (m, 10H, CH).

*2.2.10. Synthesis of mer-trans-iodo(methyl)-[(5-tertbutyl-2-oxocyclohexen-1-yl)carbonyl]-bis(trimethylphosphine)nickel (**12**)*

A sample containing 3.00 g of [(5-*tert*-butyl-2-oxocyclohexen-1-yl)carbonyl]tris(trimethylphosphine)nickel (6.42 mmol) and 2.27 g of iodomethane (16.0 mmol) in 40 ml of acetonitrile at -30°C turned from red to green within 5 min, depositing first a white and finally a yellow solid. Workup as with **4** produced a yellow powder (2.25 g, 66%), dec. >110°C.

Anal. Calc. for $C_{18}H_{37}INiO_2P_2$ (533.0): C, 40.56; H, 7.00. Found: C, 39.79; H, 6.83%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1688vs. Solution spectroscopy was not reproducible due to a fast decomposition in THF-d_8 at -60°C which was recognised from a green colour.

*2.2.11. Synthesis of mer-trans-bromo(methyl)-(1-carbonyl-2-oxo-1,2-diphenyl-diyl)-bis(trimethylphosphine)nickel (**15**)*

A sample containing 3.55 g of (1-carbonyl-2-oxo-1,2-diphenyl-diyl)tris(trimethylphosphine)nickel (6.97 mmol) and 2.00 g of bromomethane (21.1 mmol) in 50 ml of acetonitrile at -30°C turned brown within 15 min, depositing first a white and finally a yellow solid. The solids were washed with two 5 ml portions of ether and three times with water to yield, after drying in vacuo, a yellow powder (3.28 g, 89%), dec. >152°C.

Anal. Calc. for $C_{22}H_{31}BrNiO_2P_2$ (528.0): C, 50.04; H, 5.96. Found: C, 49.78; H, 5.92%.

IR (Nujol mull, ν(C=O), 2600–1600 cm^{-1}): 1693vs, 1670s. ^1H NMR (300 MHz, acetone-d_6, 243 K): δ 1.16 (t, $^3J(PH) = 8.2$ Hz, 3H, $NiCH_3$), 1.54 (t′, $|^2J(PH) + {}^4J(PH)| = 8.6$ Hz, 18H, PCH_3), 7.17 (m, 10H, CH). $^{31}P\{^1H\}$ NMR (81 MHz, THF-d_8, 233 K): δ 18.5 (s).

*2.2.12. Reaction of **11** with $CoMe(PMe_3)_4$*

A sample containing 1.75 g of **11** (3.33 mmol) and 2.52 g of $CoMe(PMe_3)_4$ (6.67 mmol) in 60 ml of ether turned from red to brown within 10 min. After 20 min the volatiles were removed in vacuo, and the residue was extracted with 80 ml of pentane over a glass-sinter disc (G3). Slowly reducing the volume of the filtrate gave dark blue crystals (400 mg) of $CoI(PMe_3)_3$ [8] (IR). Subsequent crystallisation from the mother liquor at -27°C afforded light brown crystals (549 mg, 30% based on the chelate ligand) of **13** [9] which was identified by IR and ^1H NMR spectroscopy. Among the highly soluble compounds remaining in the mother liquor $Ni(PMe_3)_4$ was detected (IR).

*2.2.13. Reaction of **12** with $CoMe(PMe_3)_4$*

In a similar procedure starting with 1.80 g of **12** (3.43 mmol) and 2.59 g of $CoMe(PMe_3)_4$ (6.86 mmol) were obtained dark blue crystals (400 mg) of $CoI(PMe_3)_3$ [8] and yellow crystals (300 mg, 15% based on the chelate ligand) of **14** [9].

*2.2.14. Reaction of **11** with $Co(PMe_3)_4$*

A sample containing 1.23 g of **11** (2.59 mmol) and 0.95 g of $Co(PMe_3)_4$ (2.62 mmol) in 50 ml of ether at -30°C turned from red to brown within 10 min. After a slight turbidity was removed by filtration the solution at -27°C afforded light brown crystals (250 mg, 18%) of **13** [9] which were identified by IR and ^1H NMR spectroscopy.

*2.2.15. Reaction of **15** with $Co(PMe_3)_4$*

A sample containing 0.92 g of **15** (1.70 mmol) and 0.63 g $Co(PMe_3)_4$ (1.74 mmol) in 50 ml of acetone formed a dark brown solution upon warming from -30 to 20°C. After evaporation to dryness the residue was extracted with ether to afford, at -27°C, red crystals of (1-carbonyl-2-oxo-1,2-diphenyl-diyl)tris-(trimethylphosphine)nickel (180 mg, 21%) which were identified by IR and ^1H NMR spectroscopy. No cobalt containing species could be identified.

*2.2.16. Reaction of **15** with $CoC{\equiv}CPh(PMe_3)_4$*

A total of 0.99 g of **15** (1.88 mmol) and 0.87 g of $Co(CCPh)(PMe_3)_4$ (1.88 mmol) in 60 ml of ether formed a brown solution upon warming from -30 to 20°C. After evaporation to dryness the residue was extracted with pentane to afford, at -27°C, red cubes of (1-carbonyl-2-oxo-1,2-diphenyl-diyl)tris(trimethyl-phosphine)nickel (280 mg, 29%) which were identified as above.

2.2.17. X-ray data

2.2.17.1. Crystal structure analysis. Crystal data for complex **7** are presented in Table 1.

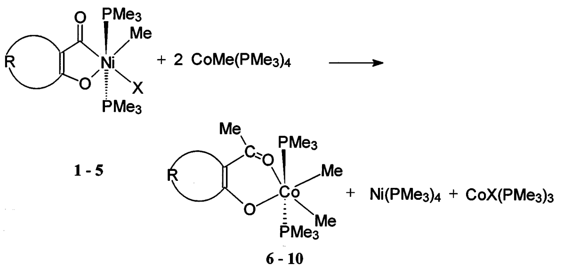
Table 1
Crystal data and refinement details for **7**

Formula	$C_{21}H_{41}CoO_2P_2$
Molecular mass	446.4
Crystal size (mm)	$0.07 \times 0.20 \times 0.65$
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	17.916(4)
b (Å)	13.734(3)
c (Å)	20.080(3)
V (Å^3)	4940.9(17)
Z	8
D_{calc} (g cm^{-3})	1.200
μ(Mo Kα) (mm^{-1})	0.836
Temperature (K)	293(2)
Data collection range (°)	2.03–27.50
Limiting indices	$-1<h<23$, $-17<k<1$, $-1<l<26$
No. reflections measured	6866
No. unique data	5675 ($R_{int} = 0.0291$)
Parameters	236
Goodness-of-fit on F^2	0.931
R_1 ($I>2\sigma(I)$)	0.0509
R_1 (all data)	0.1669
wR_2 (all data)	0.1594
$\Delta\rho_{max}$ (e Å^{-3})	0.336
$\Delta\rho_{min}$ (e Å^{-3})	-0.392

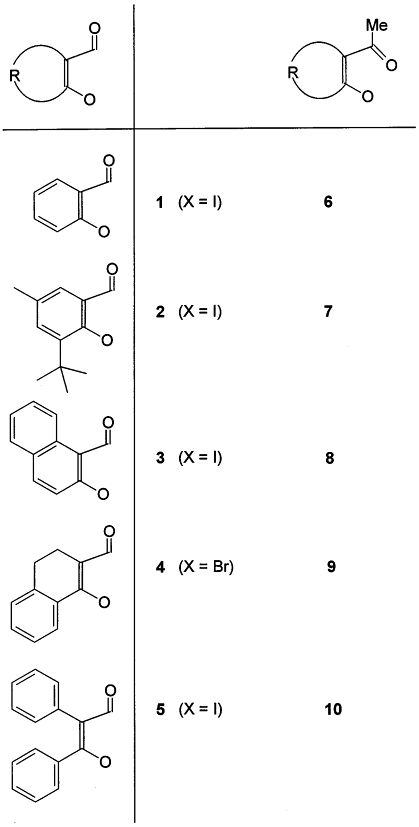
2.2.17.2. Data collection. A crystal of suitable shape was sealed in a glass capillary under argon and mounted on a diffractometer (Bruker P4). Data were collected using monochromated Mo Kα radiation. Cell constants were refined from 25 centred reflections. An absorption correction based on ψ-scans was introduced. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically on F^2. Hydrogen atoms were fixed at idealised positions with isotropic thermal parameters.

3. Results and discussion

In a second type of bidentate ligand exchange [2] following a 1:2 stoichiometry and involving acyl(methyl)nickel(IV) complexes and methylcobalt(I) compounds, the total of six anionic ligand functions becomes four through a reductive C,C-coupling reaction according to Eq. (2).

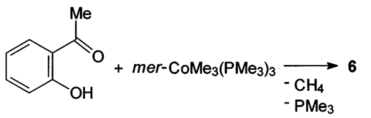


(2)



The novel oxidation/reduction transformations of ligands and complexes in ether solutions under ambient conditions require reaction times of about two days and are monitored by a slow change from a red to a red–brown coloration. Workup and separation of the three products formed by the two metals is best achieved in pentane. The almost insoluble blue microcrystals of $CoX(PMe_3)_3$ [8] are easily removed by filtration, while $Ni(PMe_3)_4$ remains in solution when the red crystals of dimethylcobalt complexes **6**–**10** are frozen out. Only in the synthesis of **6** with its exceptionally meagre yield of 27%, were small amounts of (2-oxobenzoyl)tris(trimethylphosphine)nickel [5] detected as a by-product (IR).

An independent high yield synthesis for **6** proceeds according to Eq. (3) and appears to provide the most straightforward route to this type of dimethylcobalt(III) complex starting from a 2-acylphenol [10]. Chelating coordination of the acetylic O-donor renders the overall reaction smoother than with unsubstituted phenol [6].



(3)

The molecular structure of **7** is shown in Fig. 1. The cobalt atom attains an octahedral coordination by two equatorial *cis*-methyl groups (C14–Co–C15 = 94.61(18)°

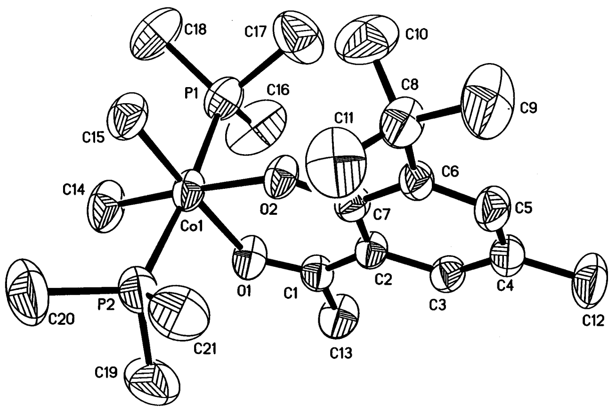


Fig. 1. Molecular structure of **7**; selected distances (Å) and angles (°): Co–O1 1.985(3), Co–O2 1.990(3), Co–C14 1.999(4), Co–C15 1.986(4), Co–P1 2.2228(17), Co–P2 2.2213(17), O1–C1 1.254(4), O2–C7 1.299(4), C1–C2 1.445(5), C1–C13 1.506(5), C2–C7 1.427(5); O1–Co–C15 176.88(15), O1–Co–O2 88.53(10), C15–Co–O2 88.36(14), O1–Co–C14 88.5(1), C15–Co–C14 94.61(18), O2–Co–C14 177.03(15), O1–Co–P2 91.67(11), C15–Co–P2 88.73(15), O2–Co–P2 92.84(10), C14–Co–P2 87.15(16), O1–Co–P1 90.20(11), C15–Co–P1 89.70(15), O2–Co–P1 92.69(10), C14–Co–P1 87.41(16), P2–Co–P1 174.21(6), C1–O1–Co 130.5(3), C7–O2–Co 129.3(2), O1–C1–C2 124.3(3), O1–C1–C13 114.1(3), C7–C2–C1 123.0(3).

opposite to the planar O:O-chelate ring of a 2-acetylphenolate anion with the usual bite-angle (O1–Co–O2 = 88.53(10)° and by two axial trimethylphosphines which are slightly bent (P1–Co–P2 = 174.21(6)°) towards the CoMe groups. Co–O and Co–C distances are as expected and fall within the range of three standard deviations (1.99(1) Å). While the 2-acetylphenolato ligand displays a shorter acyl(sp^2)C,O distance (C1–O1 = 1.254(4) Å) when compared with the phenolato(sp^2)C,O distance (C7–O2 = 1.299(4) Å), conjugational effects upon coordination shorten the original single bond C1–C2 to 1.445(4) Å and lead to similar angles at the two oxygen atoms (C1–O1–Co = 130.5(3), C7–O2–Co = 129.3(2)°).

The fate of the NiMe and CoMe groups in the transmetallation process has been investigated by deuterium labelling. Oxidative addition of CD_3I in the preparation of **2** [1] furnishes a $NiCD_3$ group in complex **2**(**D**). Crystals of **7** and **7**(**D**) were shown to be isotypical (identical lattice parameters). NMR spectra of the products of the reaction described by Eq. (2) show all the deuterium of compound **7**(**D**) to be contained in the methylketone group of the bidentate ligand. Migration of methyl groups between nickel and cobalt is thus excluded but is believed to occur between two intermediate methylcobalt complexes in a subsequent step.

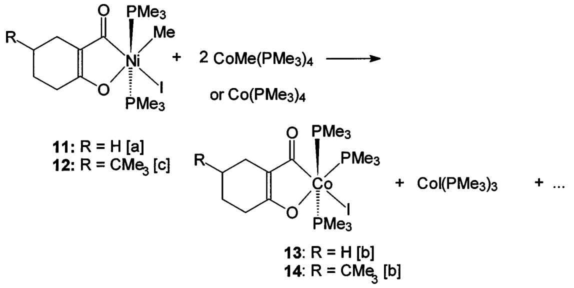
In Scheme 1 a mechanism is suggested for a product-forming sequence of four bimolecular steps.

A total of six hypothetical intermediates (A–F) is required to connect the two educts with the three products of Eq. (2). C,C-coupling is most probably initiated by single-electron transfer from a Ni(0) fragment F to the Ni(IV) educt complex (**1**–**5**) along a Ni–X–Ni bridge [1] generating intermediates A and B. After reductive elimination the resulting Ni(I) intermediate and $CoMe(PMe_3)_4$ exchange the 2-acetylphenolate ion for phosphine ligands via ring-opening and bridging coordination leading to a 17-electron species D and the 16-electron Ni(0) fragment F closing the catalytic cycle of nickel.

Formation of the Ni(0) product and a second Co(II) intermediate E is followed by transfer of a methyl group involving both Co(II) species D and E which in a dismutation reaction provide the Co(III) and Co(I) final products. Methyl group transfer reactions involving odd-electron species have been recently investigated in $(diimine)PtMe_2$ systems [10].

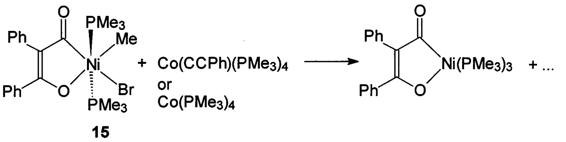
4. Miscellaneous ligand exchange reactions

When cyclohexene-type acylenolato ligands are introduced reactions under conditions of Eq. (2) unexpectedly take a different course. Without transforming an acyl into an acetyl function the anionic ligand is transferred from nickel to cobalt according to Eq. (4).



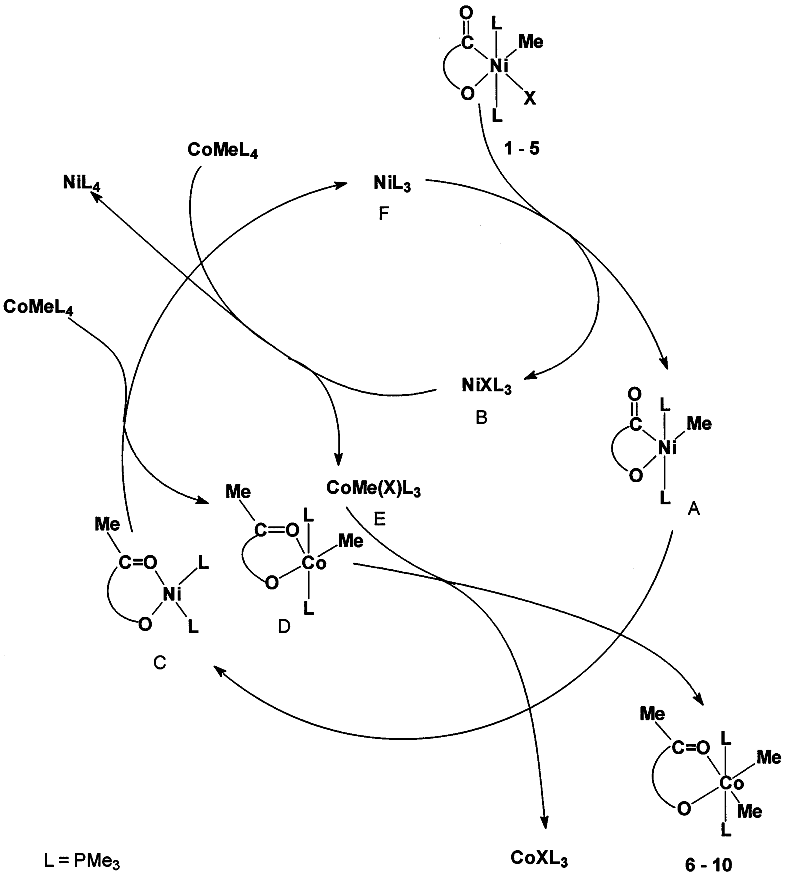
[a]: Ref. [2], [b]: Ref. [9], [c]: this work. (4)

Reaction of tetravalent nickel with low-valent cobalt complexes according to Eq. (5) does not include transfer of the chelating ligand. Any trimethylphosphine complex of cobalt in a formal oxidation state of + 1 or below appears to be capable of performing a reductive substitution reaction of **15**.



(5)

At this stage we find it difficult to predict the stoichiometries and directions of transmetallation reactions involving dianionic chelate systems. The only general trend observed here demonstrates that Co(d^6) complexes are thermodynamically more stable than Ni(d^6) complexes with a similar set of ligands.



Scheme 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data (CCDC-127451) can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@chemcrys.cam.ac.uk).

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