International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075
www.chemicaljournals.com
Volume 1; Issue 1; September 2017; Page No. 37-44

Synthesis and Characterization of Cobalt (I) & (III) Complexes containing N-(1-Naphthylmethylene) aniline and their Derivative Supported with Phosphine Ligands

Hamdi AM Bennour
Department of Chemistry, Faculty of Science, Benghazi University, Benghazi, Libya

Abstract

Cyclometalation reactions are among the oldest C-H activation processes, and those involving aromatic phosphines are well known in electron-rich complexes of the late transition metals. We have recently been able to effect cyclometalation reactions for the first time at basic cobalt centers by using imine group. It is also of general interest to study the reactivity of trimethylphosphine stabilized cobalt compounds toward aromatic imines. Imine ligands are reacts smoothly under mild conditions with cobalt (I) adducts to form five-membered metallacycles.The reaction of N-(1-naphthylmethylene) aniline, N-(1-naphthylmethylene)-2,6-dimethylaniline and N-Benzylbenzylidene imine with $CoCH_3$ $(PMe_3)_4$ to give ortho-metalated Co (I) & (III) complexes 1, 2, 3 and 4. All complexes are given from 1- 4 were characterized through IR, NMR and X-ray diffraction.

Keywords: C-H activation, cobalt, cyclometalation, N ligands

1. Introduction

Many commercially important processes that rely on transition metal organometallic complexes as catalysts have been developed, and such applications are likely to gain more importance in the future [1]. The activation of C – H bonds by “organometallic routes” (i.e., those involving the formation of a bond between carbon and a metal center) is a very large, diverse and highly active field [2, 8]. The first reported example of “C-H activation” by a transition metal complex is often attributed to Chatt [9] Ru (0) $(dmpe)_2$ was generated, leading to activation of a C-H bond of a ligand phosphine methyl group or of a C-H bond of naphthalene. C-H bond activations are often classified as proceeding via either nucleophilic (oxidative addition) or electrophilic modes. However, current directing groups, such as the well explored pyridyl moiety, can only direct the activation of C−H bonds that are close in distance and geometrically accessible, typically ortho-C−H bonds due to the chelating effect. [10−19] Perhaps even more so than the corresponding modes of H_2 activation. Both reactions appear to proceed through a σ- bond intermediate [20, 22]. Even more striking, putatively electrophilic activations, in most cases, proceed via complete oxidative addition (followed by deprotonation of the resulting metal hydride) [23]. Cyclometalation reactions are intramolecular C-H oxidative additions in which C-H bond breaking and M-C bond formation occurs for alkyl or aryl groups attached to a donor atom. The result is the formation of a heterocyclic ring. The hydrogen from C-H may in some cases remain bound to the metal, but more commonly an elimination reaction occurs in which H combines with H, Cl, or CH_3 etc. bound to the metal to generate H_2, HCl, CH_4 etc. Probably the most common intramolecular C-H oxidative addition is the so-called *ortho*-metalation reaction of aryl groups. This is of great importance in complexes of trialkylphosphine, but many substrates such as azobenzene, aromatic ketones and thioketones, or imine compounds can react similarly. Cyclometalation of ligand aryl groups was discovered early and ultimately found to be quite common [24]. Benzylic imines (PhCH=NR) are the most studied ligands in the cyclometalation of transition metals. The first examples of cyclometalated compounds of transition metals are benzylideneaniline (*N*-phenyl benzylideneimine) reactions of Pd, Mn and Re [25, 26]. Thirty years ago Bruce *et al.* studied the main part of cyclomanganation chemistry involving *N*-donor substrates and it is one of the standard procedure for activating C-H bonds ever since. Cyclometalated complexes arise from the reaction of CH_3Mn $(CO)_5$ with benzylideneani line in light petroleum by refluxing [27, 29]. Another metal which has been studied very often in reactions with imines is ruthenium [30, 33]. Ruthenium complex-catalyzed C-H olefin coupling and related reactions have been widely recognized as useful synthetic processes for carbon - carbon bond formation [34]. Hiraki observed an unusual formation of cyclometalated C, H-*trans*–hydridoruthenium (II) complex and its isomerization into C,H-*cis*-type [35]. The catalysis of organic reactions is one of the most important applications of organometallic chemistry and has been a significant factor in the rapid development of the whole field.[36] Organometallic catalysts have long been used in industrial processes but are now being routinely applied in organic synthesis as well. The application of organometallic reagents and catalysts to synthetic problems is one of the fastest growing areas [37]. Continuing rise in environmental concerns and green chemistry led to increasing interest in catalytic reactions. Study of the polymerization of olefins by soluble, well defined transition metal complexes is an ever growing area but it is already clear that these catalysts can produce polymers of quite different microstructures and could become commercially important in future [38].

2. Experimental

2.1 General procedures and materials:

All air-sensitive and volatile materials were handled either in vacuo or under argon by using standard Schlenk techniques [39]. This type of apparatus offers an opportunity of carrying out a complete synthesis in a closed system, and in one run synthesis, transport and storage of chemicals were done under an atmosphere of purified Argon (BTS catalyst) [40]. Solvents (THF, diethyl ether, and pentane) were dried according to known procedures and were freshly distilled prior to use. All reagents (Aldrich, Acros, Fluka, or Lancaster) were used as purchased without further purification.

Trimethylphosphine PMe$_3$ [41], CoMe(PMe$_3$)$_4$ [42], N-(1-naphthylmethylene)-aniline [43] and were synthesized according to literature procedures. C, H, P, N analyses of air sensitive solids were carried by H. Kolbe micro-analytical laboratory, Mulheim /Ruhr. Infrared spectra (4000-400 cm^{-1}), as obtained from Nujol mulls between KBr discs, were recorded on a Bruker FRA106 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained from Bruker AVANCE 500, ARX 300 and AM 200 spectrometers. ^{13}C and ^{31}PNMR resonances were obtained with broad-band proton decoupling. Assignment of ^{13}C signals was supported by DEPT trace. Melting points were measured in capillaries sealed under argon atmosphere.

N-(1-naphthylmethylene)-2, 6-dimethylaniline

This ligand was prepared by refluxing a mixture of 7.40 g (47.3 mmol) of α- naphthylcarbaldehyde and of 5.74 g (47.3 mmol) of 2, 6-dimethylaniline in 70 ml toluene for 6 hours. Toluene was removed in vacuo, and the residue was distilled to yield yellow oil which slowly crystallized at 4 °C. 10.20 g of a yellow solid were collected in 83% yield, m.p. 71 - 72°C (dec). ^{1}H NMR (300 MHz, d_8 -THF, 297 K, ppm): δ = 2.17 (s, 6H, Ar–CH$_3$); 6.94 (t, ^{3}JH,H = 7.7 Hz, 1H, Ar–H); 7.09 (d, ^{3}JH,H = 7.5 Hz, 1H, Ar–H), 7.58-7.69 (m, 3H, Ar–H); 8.03 (dd, ^{3}JH,H = 7.3 Hz, ^{4}JH,H = 1.5 Hz, 1H, Ar–H); 8.10 (d, ^{3}JH,H = 8.3 Hz, 1H, Ar–H); 8.14 (d, ^{3}JH,H = 7.2 Hz, 1H, Ar–H); 8.91 (s, 1H, Ar–H); 9.29 (d, ^{4}JH,H = 8.3 Hz, 1H, H–C=N). ^{13}C NMR (300 MHz, d_8 -THF, 297 K, ppm): δ = 18.1 (s, Ar–CH$_3$); 117.2 (s, CH); 123. (s, CH); 125.2 (s, CH); 125.7 (s, CH); 126.7 (s, CH); 126.9 (s, C); 127.9 (s, C); 128.4 (s, CH); 129.1(s, CH); 130.7 (s, CH); 131.8 (s, C); 132.3 (s, CH); 134.5 (s, C); 149.9 (s, C); 163.7 (s, H–C=N). C$_{19}$H$_{17}$N, Mw. (259.35 g/mol): Calc.: C, 87.99; H, 6.61; N; 5.40 Found: C, 87.60; H, 6.62; N; 5.39 %.

[2-[(phenylimino-κN)methyl]naphthyl-κC]tris-(trimethylphosphine)cobalt(I) (1)

875 mg (2.31mmol) of CoCH$_3$(PMe$_3$)$_4$ in THF were combined with 535 mg (2.31 mmol) of N-(1naphthyl methylene)aniline to afford **1** as dark green crystals, yield 981mg (82%); M.P.109 - 111 °C. (dec). IR (Nujol) $\bar{\upsilon}$ = 3048 w (ν H−C=C); 1587 m (ν C=C); 1340 w (δas PCH$_3$); 1294 m, 1277 m (δsPCH$_3$); 1191 w; 1167 m; 936 vs (ρ1 PCH$_3$); 810 w (ρ2 PCH$_3$); 767 w (γ C−H arom); 741m, 700 m (νas PC$_3$); 654 m (νs PC$_3$). ^{1}H NMR (500 MHz, d_8-THF, 300 K, ppm): δ = 1.06 (s, 27H, PCH$_3$); 7.07 (t, ^{3}JH,H = 7.3 Hz, 1H, Ar−H); 7.15 - 7.28 (m, 6H, Ar−H); 7.46 (d, ^{3}JH,H = 8.5 Hz, 1H, Ar−H); 7.64 (d, ^{3}JH,H = 8.3 Hz, 1H, Ar−H); 7.97 (d, ^{3}JH,H = 8.3 Hz, 1H, Ar−H); 8.39 (d, ^{3}JH,H = 8.5 Hz, 1H, Ar−H); 9.51 (sbr, 1H, H−C=N). ^{13}C NMR (125 MHz, d_8 -THF, 300 K, ppm): δ = 22.3 (m, PCH$_3$); 112.2 (s, CH); 121.8 (s, CH); 122.1 (s, CH); 123.7 (s, CH); 124.1 (s, CH); 126.6 (s, CH); 127.5 (s, CH); 131.3 (s, CH); 141.1 (s, C); 142.6 (s, C); 145.8 (s, C); 153.3 (s, C); 158.6 (s, C=N); 179.2 (m, Co-C). ^{31}P NMR (202 MHz, d_8 -THF, 300 K, ppm): δ = -16.3 (m, 2P, PCH$_3$); - 3.8 (m, 1P, PCH$_3$). C$_{26}$H$_{39}$CoNP$_3$, Mw. (517.46 g/mol): Calc.: C, 60.35; H, 7.60; N; 2.71; P, 17.96 Found: C, 60.12; H, 7.86; N; 2.71; P, 17.95 %.

[2-[(2,6-dimethylphenylimino-κN)methyl]naphthyl-κC]tris(trimethylphosphine)cobalt(I) (2)

A solution of N-(1-naphthylmethylene)-2,6-dimethylaniline (0.994 g, 3.83 mmol) in 10 mL of THF were combined with a solution of CoCH$_3$(PMe$_3$)$_4$ (1.45 g, 3.83 mmol) in THF (50 mL) at -80 °C. This was allowed to warm to 20 °C and stirred for 18 h to form a green, turbid mixture, which was filtered. Crystallization from pentane at -27 °C yielded dark green single crystals **2** suitable for X-ray analysis; yield 1.25 g (60%), M.P.109 - 111 °C. (dec). IR (Nujol) $\bar{\upsilon}$ = 3047 w (ν H−C=C); 1637 vw; 1606 vw, 1590 vw (ν C=C); 1531 vw (ν C=N); 1423 m (δas PCH$_3$); 1327 m; 1318 m; 1296 m, 1275 s (δs PCH$_3$); 1253 vw; 1187 m; 1143 vw; 1092 vw; 1042 vw; 956 s, 940 vs (ρ1 PCH$_3$); 875 w; 845 w (ρ2 PCH$_3$); 818 w; 804 s, 760 s (γ C− H arom); 734 m; 697 m (νas PC$_3$); 664 m (νs PC$_3$); 624 vw; 599 vw; 571 vw; 542 vw; 503 vw; 460 w; 436 w; 417 w. ^{1}H NMR (500 MHz, *d8* -THF, 300 K, ppm): δ = 1.01 (sbr, 9H, PCH$_3$); 1.07 (s, 18H, PCH$_3$); 2.14 (s, 6H, Ar − CH$_3$); 7.02 - 7.08 (m, 4H, Ar − H); 7.18 (t, ^{3}JH,H = 7.4 Hz, 1H, Ar − H); 7.48 (d, ^{3}JH,H = 8.2 Hz, 1H, Ar − H); 7.64 (d, ^{3}JH,H = 7.9 Hz, 1H, Ar − H); 7.94 (d, ^{3}JH,H = 8.2 Hz, 1H, Ar − H); 8.53 (d, ^{3}JH,H = 8.6 Hz, 1H, Ar − H); 9.34 (s, 1H, H− C = N). ^{13}C NMR (125 MHz, d_8 - THF, 300 K, ppm): δ = 19.1 (s, Ar − CH$_3$); 23.3 (dt, ^{3}JP,C = 2.2 Hz, ^{1}JP, C = 10.6 Hz, PCH$_3$)118.9 (dd, ^{5}JP,C = 3.4 Hz, ^{4}JP,C = 5.6 Hz, CH); 122.8 (s, CH); 123.4 (s, CH); 124.9 (d, ^{5}JP,C = 4.5 Hz, CH); 128.6 (s, CH); 128.8 (s, CH); 131.8 (s, C); 132.5 (s, C); 133.6 (s, C); 138.9. (s, C); 142.8 (s, C); 144.4 (m, CH); 153.3 (m, CH); 160.4 (d, ^{4}J P,C = 3.4 Hz, C=N); 181.2 (m, Co − C). ^{31}P NMR (202 MHz, d_8 -THF, 300 K, ppm): δ = -14.9 (sbr, 2P, PCH$_3$); -4.5 (sbr, 1P, PCH$_3$). C$_{28}$H$_{43}$CoNP$_3$ (545.51 g/mol): Calc.: C, 61.76; H, 7.77; N, 2.57; P, 17.07 Found: C, 60.61; H, 7.86; N, 2.64; P, 17.35%.

Hydrido[2-[((2-Benzyl-κC)imino-κN)methyl]phenyl-κC]tris-(trimethylphosphine)cobalt(III) (3)

A solution of *N* benzyl-benzylideneimine (434 mg, 2.22 mmol) in 20 mL of THF were combined with a solution of CoCH$_3$ (PMe$_3$)$_4$ (840 mg, 2.22 mmol) in THF (50 mL) at -80 °C. This was allowed to warm to 20 °C and stirred for 18 h to form an orange, turbid mixture, which was filtered. Crystallization from pentane at 4 °C yielded orange single crystals **3**; yield 99 mg (11%), M.P.116 - 118 °C. (dec). IR (Nujol) $\bar{\upsilon}$ = 3096 vw, 3069 vw (ν H−C=C); 1879 m (ν Co−H); 1588 w, 1573 s (ν C=C); 1531 w (ν C=N); 1427 m, 1416 m (δas PCH$_3$); 1309 w, 1298 w (δs PCH$_3$); 1274 s; 1254 vw; 1204 w; 1149 vw; 1109 w; 1056 w; 1020 vw; 1005 w; 936 vs (ρ1 PCH$_3$); 855 s, 841 s (ρ2 PCH$_3$); 811 vw; 756 s (γ C−Harom); 726 vs (νas PC$_3$); 670 m (νs PC$_3$); 619 vw; 535

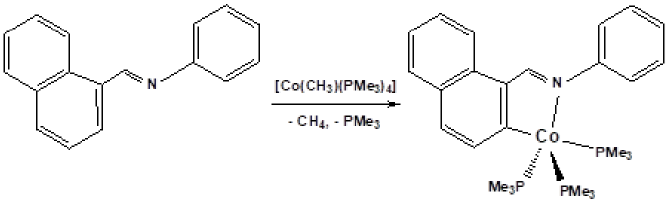
vw; 477 vw; 458 vw. ^{1}H NMR (500 MHz, d_8 -THF, 300 K, ppm): δ = - 18.73 (t, ^2JP,H = 72.4 Hz, 1H, Co−H); 0.80 (s, 27H, PCH_3); 5.08 (s, 2H, CH_2); 6.69 (m, 1H, Ar − H); 6.72 (t, ^3JH,H = 6.8 Hz, 1H, Ar−H); 6.80 (d, ^3JH, H = 6.8 Hz, 1H, Ar − H); 6.85 (t', ^3JH,H = 6.9 Hz, 1H, Ar-H); 6.91 (t, ^3JH,H = 6.8 Hz, 1H, Ar − H); 7.29 (d, ^4JP,H = 5.3 Hz, 1H, Ar − H); 7.39 (d, ^3JH,H = 7.1 Hz, 1H, Ar − H); 7.63 (d; ^3JH,H = 6.5 Hz, 1H, Ar − H); 8.56 (s, 1H, H− C=N). ^{13}C NMR (125 MHz, d_8 -THF, 300 K, ppm): δ = 17.7 (t', |^1JP,C + ^3JP,C| = 29.6 Hz, PCH_3); 64.4 (s, CH_2); 119.6 (t, ^5JP,C = 2.3 Hz, CH); 120.8 (s, CH); 121.4 (t, ^5JP,C = 2.2 Hz, CH); 124.9 (t, ^5JP,C = 3.4 Hz, CH); 126.6 (s, CH); 126.9 (s, CH); 145.9 (s, CH); 146 (d, ^5JP,C = 2.0 Hz, CH); 151.3 (m, C); 152.1(s, C); 166.8 (t, ^3JP,C = 3.61 Hz, C=N); 176.7 (m, Co − C); 194.6 (m, Co − C). ^{31}P NMR (202 MHz, d_8 -THF, 300 K, ppm): δ = 9.98 s, PCH_3. C20H30CoNP2, (405.35g/mol): Calc.: C, 59.26; H, 7.46; N, 3.46; P, 15.28 Found: C, 59.11; H, 7.71; N, 3.84; P, 16.79 %.

(η^3-κC,κN,κC)[[[(Phenylmethyl)imino]methyl]phenyl]tris-(trimethylphosphine)cobalt(I) (4)

A solution of *N* benzyl-benzylideneimine (434 mg, 2.22 mmol) in 20 mL of THF were combined with a solution of $CoCH_3(PMe_3)_4$ (840 mg, 2.22 mmol) in THF (50 mL) at -80 °C. This was allowed to warm to 20 °C and stirred for 18 h to form an brown, turbid mixture, which was filtered. Crystallization from pentane at 4 °C yielded brown single crystals **4**; yield 568 mg (58%), M.P. 115 - 117 °C. (dec). IR (Nujol) ῡ = 3073 vw, 3055 w, 3018 m (ν H−C=C); 1591 vs (ν C=C); 1486 s (ν C=N); 1425 s (δas PCH_3); 1294 m, 1275 m (δs PCH_3); 1245 w; 1220 w; 1153 w; 1140 w; 1063 m; 1024 w; 996 vw; 953 vs, 936 vs (ρ1 PCH_3); 847 m (ρ2 PCH_3); 756 vs γ(C−Harom); 699 vs (νas PC_3); 657 vs (νs PC_3); 636 w; 627 vw; 611 vw; 575 m; 527 m; 505 vw; 419 vw. ^{1}H NMR (500 MHz, d_8 - THF, 300 K, ppm): δ = 1.06 (s, 27H, PCH_3); 2.21 (sbr, 1H, NCH); 7.03 (m, 6H, Ar−H); 7.66 (m, 4H, Ar−H). ^{13}C NMR (125 MHz, d_8 - THF, 300 K, ppm): δ = 22.8 (m, PCH_3); 64.1 (s, N−CH); 124.0 (s, CH); 128.6 (s, CH); 128.8 (s, CH); 150.1 (s, C). ^{31}P NMR (202 MHz, d_8 - THF, 300 K, ppm): δ = - 5.3 (s, PCH_3). C_{23} H_{39} Co N P_3, (481.39g/mol): Calc.: C, 57.33; H, 8.10; N, 2.09; P, 19.26 Found: C, 57.59; H, 7.97; N, 2.82; P, 19.27 %.

3. Results and discussion

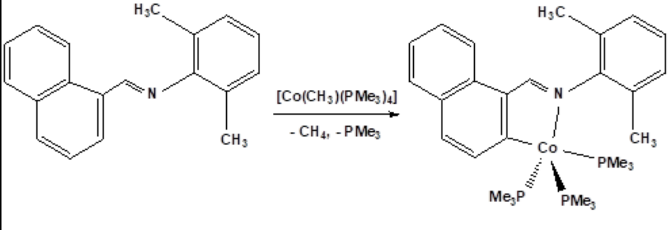
N-(1naphthylmethylene) aniline reacts with $CoCH_3$ $(PMe_3)_4$ at -70 °C [Eq.1] to afford **1** exclusively, isolated in 82 % yield. Concentrated pentane solutions afforded at – 27 °C dark green crystals of **1**. Figure 1. Synthesis of complex 1



1

Fig 1: Synthesis of complex 1

The most distinctive spectroscopic data in the IR spectrum are a bathochromic shift of 127 cm $^{-1}$ for the imine band in comparison with the free ligand. In the ^{13}C NMR spectrum of the *ortho*-metalated complex 1 only one metallated carbon can be detected at 197.2 ppm as a multiplet. The ^{31}P NMR shows two resonances at -16.3 ppm and -3.8 ppm as multiplets. Even at -100 °C the coupling pattern cannot be resolved, which is either due to dynamic behaviour of the complex or quadropol broadening (ICo=7/2). In ^{31}P NMR the phosphorus nuclei appear as two resonances because of the low symmetry of the chelating ligand. The switched [C, N] coordination mode in the imine ligand gives the same result as observed in the reaction with a dimethyl iron complex. Again no bicyclometalation is observed which is due to the steric demand in the second C-H activation step forming a four-membered metallacycle. Here the reaction sequence does not involve a reductive elimination step because the methyl group is eliminated in the first step of the cobalt complex. A possible mechanism of the reaction may start by dissociation of a phosphine group and coordination of cobalt to the nitrogen atom. Proximity of the cobalt atom towards the *ortho* C-H bond is affected by σ - or π - coordination. Activation and regiospecific cleavage of the C-H bond forms a hydrido-cobalt (III) compound which eliminates methane (1-naphthylmetylene)-2, 6-dimethylaniline providing one in plane *ortho*-C(sp^2)-H and one *ortho*-C(sp^3)-H bond out of plane, reacts with $Co(CH_3)$ $(PMe_3)_4$ at -70 °C with a gas evolution [Eq.2] to afford **2** exclusively, isolated in 60 % yield, as dark green crystals.



2

Fig 2: Synthesis of complex 2.

The coordinated imine band is present at 1531 cm^{-1} with a bathochromic shift of 91cm^{-1} in comparison with the free imine ligand. The coordinated trimethylphosphine ligands are indicated by two broad singlet resonances at 1.01 ppm and 1.07 ppm. The six methyl protons appear at 2.14 ppm indicating no C-H activation of the methyl group. A typical low field shift is recognized for the imine proton at 9.34 ppm. In the ^{13}C NMR spectrum all resonances are found to be consistent with an *ortho-metalated* coordination sphere. The metallated aromatic carbon is shifted to 181.2 ppm and forms a multiplet. Due to the asymmetric aromatic backbone the trimethylphosphine ligands are anisochronic in solution, indicated by two resonances at –14.9 ppm for the two equatorial trimethylphosphine ligands and at - 4.5 for the axial phosphine ligand. Single crystals of 2 suitable for X-ray diffraction (Fig.1) were obtained by crystallization from pentane at - 27 °C. The crystal belongs to the space group *P*bca. The coordination of the cobalt atom can be described as a trigonal bipyramid with an axial C1 atom and an axial PMe_3

group (P3). The equatorial positions are occupied by the nitrogen atom (N1) next to the other remaining phosphine groups with the phosphorus atoms (P1 and P2). The angles from the axial (P2) to the equatorial phosphorus atoms are similar with 95.22(2)° for (P1) and 94.71(2)° for (P3), respectively. The two equatorial cobalt phosphorus distances (Co1-P1 = 2.1915(15) and Co1-P3 = 2.2030(6) Å) are shorter than those opposite the σ-bonded aryl group (Co1-P2 = 2.2401(6) due to a strong *trans* influence of the carbon atom. The distance between cobalt and nitrogen (1.9552(14) Å) is in the range for single bonds.[44] The Co-C, Co-P and P-C bond lengths are close to the average of reported values in aryl cobalt compounds. The sum of internal angles in the metallacycle (539.7°) equals that of a regular pentagon.

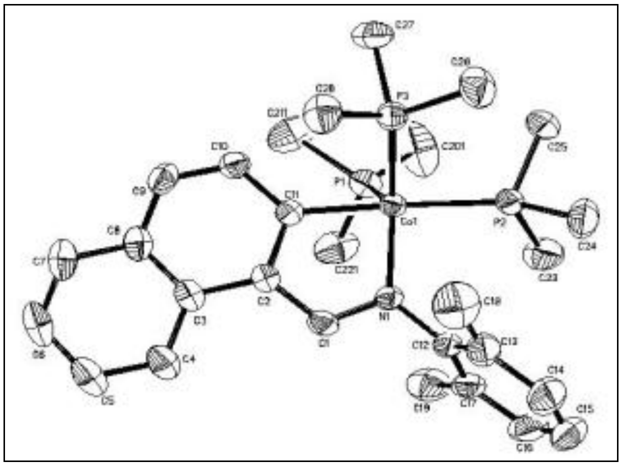


Fig 3: Molecular structure of **2** (ORTEP plot with hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Co1-C11 1.9536 (18), Co1-N1 1.9552 (14), Co1-P1 2.1915 (6), Co1-P3 2.2030 (6), Co1-P2 2.2401 (6), N1-C1 1.318 (2); C11-Co1-N1 81.06 (7), C11-Co1-P2 177.17 (6),C11- Co1-P1 84.86 (6), N1-Co1-P1 118.84 (5), C11-Co1-P3 87.82 (6), N1-Co1-P3 123.97 (5), P1-Co1-P2 95.22 (2), P3-Co1-P2 94.71 (2) P1-Co1-P3 114.47 (2).

With N-(1-naphthylmetylene)-2, 6-dimethylaniline in reaction with Co (CH_3) $(PMe_3)_4$ bicyclometallation is not possible. The reaction stops at the ortho-metallation of the β-position in the naphthyl part forming a five-membered metallacycle and no further C-H activation step of the methyl groups in the aromatic backbone occurs. Bicyclometallation reactions only occur when the two C-H bonds, which will be activated, are aromatic. It is known that many transition metals predominantly activate the stronger aryl CH bond (110 kcal/mol), instead of the weaker aliphatic C-H bond (96 – 102 kcal/mol) [45].

The reaction between Co (CH_3) $(PMe_3)_4$ and N-benzyl benzylideneimine proceeds below 20 °C according **[Eq.3].** The first step of the reaction is a bicyclometalation by a loss of methane and trimethylphosphine generating a hydrido-cobalt (III) complex 3, followed by a reductive elimination producing a π- allylic η^3-cobalt (I) complex 4.

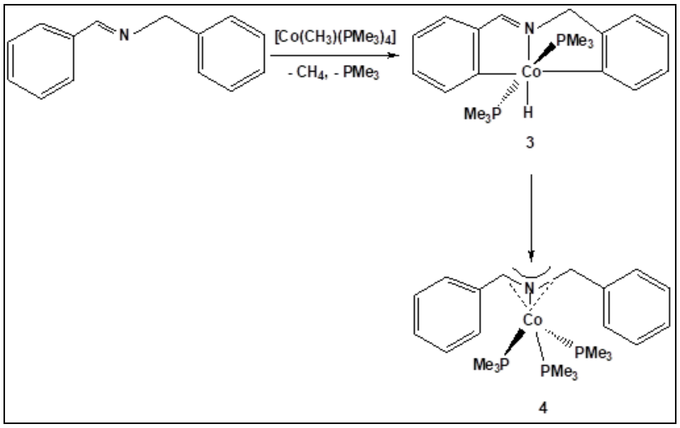


Fig 4: Synthesis of complex 3 and 4.

The reaction sequence is depending on increased reaction time and polarity of the solvent. Predominantly long reaction times and polar solvent e.g. THF provides compound 4. Both complexes crystallize from pentane at -27 °C in 11 % yield for **3** and 58 % yield for **4.** The two products formed large crystals which were separated manually. Crystals of 4 were suitable for an X-ray structure determination [Fig.4]. Most remarkable, the IR spectrum of 3 shows a broad signal at 1879 cm^{-1} indicating a cobalt-hydrid stretching frequency. Corresponding to the IR, in the ^{1}NMR spectrum with a high field shift a triplet arises for the hydrid resonance at -18.7 ppm with a ^2J(PH) coupling of 72.4 Hz. The two isochronic trimethylphosphine ligands resonate at 0.80 ppm as a singlet, the methylene protons at 5.08 ppm as a singlet and the imine proton with a typical low field shift to 8.56 ppm, next to the remaining aromatic proton signals at 6.69 - 7.39 ppm. Most significantly in the ^{1}H NMR of complex 4, is the absence of a hydrid resonance at high field and accordingly the Co-H band in the IR spectrum is not present anymore. The ^{1}H NMR and ^{13}CNMR pattern in the aromatic region suggest a more symmetric molecule. The ratio of trimethylphosphine and aromatic protons has changed from 2:1 in complex 3, to 3:1 in 4. An X-ray structure analysis of 4 which given below was carried out using a single crystal sealed in a capillary. The structure was solved by direct methods using SHELXS-97 and refined on F2 by full-matrix least-squares techniques using SHELXL-97. Cobalt, phosphorus and carbon atoms were refined anisotropically and all nitrogen atoms isotropically. The structure was solved with the space group P$\bar{1}$ with a R-value 0.1606.

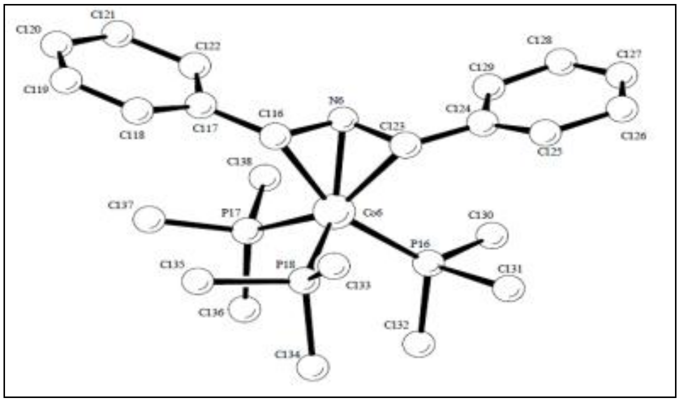


Fig 5: Molecular structure of ***4***. Selected bond lengths (Å) and angles (°): Co6-N6 1.985 (8), Co6-C123 2.099 (9), Co6-C116 2.123 (9), Co6-P16 2.222 (4), Co6-P17 2.233 (3), Co6-P18 2.231 (3), N6-C116 1.420 (11), N6-C123 1.420 (11), C116-C117 1.493 (13); C116-Co6-P16 158.9 (3), N6-Co6- P18 125.3 (3), C123-Co6-P17 146.9 (3), N6-Co6-P16 119.1 (3), N6-Co6-P17 108.8 (2), P16-Co6-P17 94.87 (16), P16-Co6-P18 100.5 (2), P17-Co6-P18 103.26 (16).

The molecular structure of 4 shows a piano stool type configuration of complex. The cobalt center is surrounded by three trimethylphosphine groups and an η^3 [C, N, C] coordination mode of anionic N benzylidenephenylimine ligand forming a π-allylic coordination to the metal like in half sandwich complexes. Regarding the midpoint [C, N, C] as a ligand position the resulting geometry of the cobalt center can be described as pseudotetrahedral. Three basal positions are occupied by the trimethylphosphine donor atoms. The C116-C117 and C123-C124 bond length (1.493(13) Å) agree well with the average carbon single bond distances in imino groups while distances N6-C116 = 1.420(11) Å and N6-C123 = 1.420(11) Å indicate a delocalized anionic ligand function. The source for the poor yield of *3* (11%) is explained by the concominant transformation to *4*.The Co-H function together with the methylene group of benzylideneimine initiate the reductive elimination of two Co-C bonds forming an η^3-coordinated cobalt I complex of Cs-symmetry. we have an example for reductive C, H elimination in a cobalt (III) intermediate to form complex *4*.

4. Conclusion

This project introduces some novel imine chelating systems of cobalt. Their model characters for the homogenous catalysis make them very interesting and attractive. Their regioselective *ortho*-metalations make a particular attention on them for the synthesis of organic compounds. Meridional bicyclometalation reactions are a novel way of forming dianionic [CNC] – ligands. Demetalation steps in bicyclometalation reactions give the possibility to synthesize organic compounds which are not accessible by classical methods.

Table 1: Crystal data for compound 1

Empirical formula	C28 H43 Co N P3
Formula weight	545.47
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 9.2326(3) Å α= 90°.
	b = 18.5977(7) Å β= 90°.
	c = 34.0872(12) Å γ = 90°.
Volume	5852.9(4) Å3
Z	8
Density (calculated)	1.238 Mg/m3
Absorption coefficient	0.767 mm-1

F(000)	2320
Crystal size	0.40 x 0.38 x 0.35 mm3
Theta range for data collection	2.19 to 28.20°.
Index ranges	-11<=h<=12, -24<=k<=24, -45<=l<=44
Reflections collected	58842
Independent reflections	7206 [R(int) = 0.0503]
Completeness to theta = 28.20°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.980 and 0.806
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7206 / 15 / 340
Goodness-of-fit on F2	0.984
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0807
R indices (all data)	R1 = 0.0633, wR2 = 0.0865
Largest diff. peak and hole	0.463 and -0.155 e.Å-3

Table 2: Crystal data for compound 4.

Empirical formula	C23 H39 Co N P3
Formula weight	481.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 15.4413(13) Å α= 90.20(2)°.
	b = 19.1241(10) Å β= 89.93(2)°.
	c = 26.8570(12) Å γ = 90.18(2)°.
Volume	7.9308(9) nm3
Z	12
Density (calculated)	1.210 Mg/m3
Absorption coefficient	0.840 mm-1
F(000)	3072
Crystal size	0.17 x 0.20 x 0.42 mm3
Theta range for data collection	1.52 to 29.55°.
Index ranges	-18<=h<=21, -26<=k<=26, -37<=l<=36
Reflections collected	123946
Independent reflections	43020 [R(int) = 0.1416]
Completeness to theta = 29.55°	96.90%
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	43020 / 0 / 1483
Goodness-of-fit on F2	1.718
Final R indices [I>2sigma(I)]	R1 = 0.1606, wR2 = 0.3607
R indices (all data)	R1 = 0.2532, wR2 = 0.3902
Largest diff. peak and hole	2.968 and -2.839 e.Å-3

Acknowledgement

The author is grateful to Prof. H. Schmidt for providing laboratory facilities, to Prof. K. Albert for a part of the crystallography. Thanks to Dr. P.K. for laboratory helping. Thanks are also offered to Prof. Mohamed Nazar Ibrahim for his interest and article reviewed, deep grateful to Ms. M. D. Elshiki for her interest and encouragement.

5. Reference

1. Cornils B, WA Hermann. Applied Homoenous Catalysis with Organometallic Compounds: A Comprehensive Handbook, VCH, New York, 1996.
2. Goldberg KI, Goldman AS. Activation Functionalization of C-H Bonds, ACS Symposium Series, 2004; 885,43.
3. Sen A. Catalytic Functionalization of Carbon−Hydrogen and Carbon-Carbon Bonds in Protic Media, Acc. Chem. Res. 1998, 31(9):550-557.
4. Guari Y, Sabo-Etiennne S, Chaudret B. Catalytic Formation of Carbon–Carbon Bonds by Activation of Carbon–Hydrogen Bonds, Eur. J. Inorg. Chem. 1999, 1047-1055.
5. WD Jones. Conquering the carbon-hydrogen bond. Science, 2000; 287:1942-1943.
6. Crabtree RH. Alkane C-H activation and functionalization with homogeneous transition metal catalysts: a century of progress-a new millennium in prospect, J. Chem. Soc. Dalton Trans. 2001; 17:2437-2450.
7. Labinger JA, Bercaw JE. Understanding and exploiting C-H bond activation. Nature, 2002; 417:507-514.
8. Ritling V, Sirlin C, Pfeffer M, Ru-Rh-, Pd- catalyzed C-C bond formation involving C-H activation and addition on unsaturated substrates: reactions and mechanistic aspects. Chem. Rev. 2002, 102:1731-1769.

9. Chatt J, JM Davidson. The Tautomerism of Arene and Ditertiary phosphine Complexes of Ruthenium (0), and the Preparation of New Types of Hydrido-Complexes of Ruthenium (II), J. Chem. Soc., 1965, 843-855.
10. Ryabov A. Mechanisms of intramolecular activation of carbon-hydrogen bonds in transition-metal complexes. Chem. Rev., 1990; 90:403-424.
11. Lim Y, Kim Y, Kang J. Rhodium-catalysed regioselective alkylation of the phenyl ring of 2- phenylpyridines with olefins. J. Chem. Soc., Chem. Commun., 1994, 2267-2268.
12. Chatani N, Ie Y, Kakiuchi F, Murai S. Ru (CO)-Catalyzed reaction of pyridylbenzenes with carbon monoxide and olefins. Carbonylation at a C-H Bond in the benzene ring. J. Org. Chem. 1997, 62:2604-2610.
13. Oi S, Fukita S, Hirata N, Watanuki N, Miyano S, Inoue Y. Ruthenium complex-catalyzed direct ortho arylation and alkenylationof 2- arylpyridines with organic halides. Org. Lett. 2001; 3:2579-2581.
14. Dick AR, Hull KL, Sanford MS. A highly selective catalytic method for the oxidative functionalization of C−H bonds. J. Am. Chem. Soc., 2004; 126:2300-2301.
15. Shabashov D, Daugulis O. Catalytic coupling of C-H and C-I bonds using pyridine as a directing group. Org. Lett. 2005; 7:3657-3659.
16. Chen X, Hao XS, Goodhue CE, Yu J-Q. Cu (II)-catalyzed function alizations of aryl C-H bonds using O_2 as an oxidant. J. Am. Chem. Soc., 2006; 128:6790-6791.
17. Chen X, Goodhue CE, Yu JQ. Palladium-catalyzed alkylation of sp^2 and sp^3 C-H bonds with methyl boroxine and alkyl boronic acids: two distinct C-H activation pathways. J. Am. Chem. Soc., 2006; 128:12634-12635.
18. Wang X, Truesdale L, Yu JQ. Pd (II)-catalyzed ortho trifluoromethylation of arenes using TFA as a promoter. J. Am. Chem. Soc., 2010; 132:3648-3649.
19. Wang X, Yu DG, Glorius F. Cp* Rh (III)-Catalyzed Arylation of C (sp^3) -H Bonds. Angew. Chem., Int. Ed., 2015; 54:10280-10283.
20. GJ Kubas, RR Ryan, BI Swanson, PJ Vergamini, HJ Wasserman. Characterization of the first examples of isolable molecular hydrogen complexes, M $(CO)_3$ $(PR_3)_2$ (H_2) (M = molybdenum or tungsten; R = Cy or isopropyl). Evidence for a side-on bonded dihydrogen ligand J. Am. Chem. Soc., 1984; 106:451-452.
21. GJ Kubas. Molecular hydrogen complexes: coordination of a sigma. bond to transition metals Acc. Chem. Res. 1988; 21(3):120-128.
22. WD Jones. Isotope Effects in C−H Bond Activation Reactions by Transition Metals, Acc. Chem. Res. 2003; 36(2):140-146.
23. SS Stahl, JA Labinger, JE Bercaw. Exploring the Mechanism of Aqueous C−H Activation by Pt (II) through Model Chemistry: Evidence for the Intermediacy of Alkyl hydridoplatinum (IV) and Alkane σ-Adducts, J. Am. Chem. Soc., 1996; 118(25):5961-5976.
24. MA Bennett, DL Milner, Chlorotris triphenylphosphine iridium (I): an example of hydrogen transfer to a metal from a co-ordinated ligand, Chem. Commun., 1967; 581-582.
25. Bennett RL, Bruce MI, Matsuda I, Doednes RJ, JT Veal. Ortho-metallation of a sulphur-donor ligand: preparation structure of $C_6H_4CH_2SMeMn$ $(CO)_3$ (PPH_3) J. Organomet. Chem. 1974; 67(3)C72-C74.
26. RL Bennett, MI Bruce FGA Stone. Cyclometallation reactions XII. On the effect of various leaving groups on internal metallation reactions with alkyl manganese complexes J. Organomet Chem., 1975; 94:65-74.
27. Bennett RL, Goodall BL, Matsuda I. Cyclometallation reactions. XIII. Reactions of phenyl- substituted heterocyclic nitrogen-donor ligands, Aust. J. Chem. 1975; 28(6):1259-1264.
28. Bennett RL, Bruce MI, Goodall BL. FGA Stone, Cyclometallation reaction ds. VIII. Binuclear manganese carbonyl complexes derived from azobenzene**,** Aust. J. Chem. 1974; 27(10):2132-2133.
29. Bruce MI, Liddell MJ, Snow MR, ERT. Tienkink, Cyclometallation Reactions. XXI. Some Chemistry of Binuclear Manganese Complexes Derived From Azobenzene: X-Ray Crystal-Structures of $\{Mn\ (CO)_4\}_2$ $(\mu\text{-}C_6H_4N{=}NC_6H_4)$ and $\{Mn\ (CO)_4\}$ $\{Mn\ (CO)_3$ $[P(OPh)_3]\}$ $(\mu\text{-}C_6H_4N{=}NC_6H_4)$ Aust. J. Chem., 1988; 41:1407-1415.
30. Martin GC, Boncella JM, Wucherer EJ. Synthesis of ruthenium amide complexes by nucleophilic attack on ortho-metalated imine ligands, Organometallics, 1991; 10(8):2804-2811.
31. Werner H, Daniel T, Knaup W, Nürnberg O. Aren- und cyclopentadienyl-halbs and wichkomplexe des rutheniums mit oximaten, carboxylaten, iminen und azavinylidenen als liganden J. Organomet. Chem., 1993; 462:309-318.
32. Hiraki K, Kinoshita Y, Ushiroda H, Koyama S, Kawano H. New Types of Coupling Reactions of Some Nitriles on Ruthenium Complexes, Chem. Lett., 1997; 12:1243-1244.
33. Flower KR, Pritchard RG, Warren JE. Synthesis of $[RuX(CO)\ \{\eta^2\text{-}C,N\text{-}C_6H_4C\ (H){=}NC_6H_4\text{-}4\text{-}NO_2\}\ (PPh_3)_2]$ (X = F, Cl, Br, I): Evidence of Non-Conventional Ru−X Hydrogen Bonds Leading to Octahedral Coordination at the Halide Atom, Eur. J. Inorg. Chem., 2003; 10:1929-1938.
34. Murai S, Kakiuchi F, Sekine S, Tanaka Y, Kamatani A, Sonoda M, Chatani N, Efficient catalytic addition of aromatic carbon-hydrogen bonds to olefins, Nature 1993; 366:529-531.
35. Hiraki K, Koizumi M, Kira S, Kawano H, Unusual Formation of Cyclometallated C, H-trans-Hydridoruthenium (II) Complexes and Their Isomerization into C,H-cis-Types Chem. Lett. 1998; 27(1):47-48.
36. Sánchez-Delgado RA, Rosales M. Kinetic studies as a tool for the elucidation of the mechanisms of metal complex-catalyzed homogeneous hydrogenation reactions, Coord. Chem. Rev., 2000; 196(1)249-280.
37. Seebach D. Organic Synthesis-Where now? Angew. Chem. Int. Ed. 1990; 29(11):1320-1367.
38. GJP Britovsek, VC Gibson, DF Wass. The Search for New-Generation Olefin Polymerization Catalysts: Life beyond Metallocenes, Angew. Chem. Int. Ed. 1999; 38(4):428-447.
39. McNally JP, Leong S, Cooper NJ. In Experimental

Organometallic Chemistry; Wayda, AL, Darensbourg, MY, Eds.; American Chemical Society: Washington, DC, Chapter, 2, 1987.

40. Schütze M. Feinreinigung von Gasen mit einem hochaktiven Kupferkatalysator, Angew. Chem., 1958; 70:697-699.
41. Wolfsberger W, Schmidbaur H. Eine Befriedigende Darstellungsmethode für Trimethylphosphin. Syn. React. Inorg. Metal-Org.Chem, 1974; 4:149-156.
42. Klein H-F, Karsch HH. Methylkobaltverbindungen mit nicht chelatisierenden Liganden, I. Methyltetrakis trimethylphosphin kobalt und seine Derivate, Chem. Ber., 1975; 108:944-955.
43. Imhof W. Reactivity of Naphthylimines toward $Fe_2(CO)_9$: Observation of Three Different Hydrogen Migration Pathways[#], Organometallics, 1999; 18(23):4845-4855.
44. Mindiola DJ, Hillhouse GL. Terminal Amido and Imido Complexes of Three-Coordinate Nickel, J. Am. Chem. Soc., 2001; 123(19):4623-4624.
45. Shilov AE, Shul'pin GB. Activation of C-H Bonds by Metal Complexes N. N. Semenov Chem. Rev., 1997; 97(8):2879-2932.