



Cite this: *Dalton Trans.*, 2014, **43**, 14696

Received 18th June 2014,
Accepted 12th August 2014
DOI: 10.1039/c4dt01823k

www.rsc.org/dalton

C–H bond activation and S-atom transfer from cobalt(III) thiolate and isothiocyanate complexes†

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The cobalt phenylthiolate complex, *cis,mer*-(PMe₃)₃Co(CH₃)₂SPh, was found to undergo competitive two-electron ethane reductive elimination and C–H bond cyclometallation. The thiophenolato bound cobaltacycle was generated *via* C–H bond oxidative addition to a five-coordinate intermediate followed by rapid methane elimination. A related cobalt isothiocyanate complex, *cis,mer*-(PMe₃)₃Co(CH₃)₂NCS, was also prepared and found to perform ethane elimination and S-atom transfer to yield trimethylphosphine sulfide. This rare example of S-atom donation from a isothiocyanate was characterized by NMR and GC-MS analysis, with *cis,mer*-(PMe₃)₃Co(CH₃)₂CN identified as one of the cobalt based products.

Introduction

Over the past few decades, the mechanism of carbon–carbon bond reductive elimination at platinum group metals has been extensively studied owing to its crucial role in many catalytic processes, such as cross-coupling.^{1,2} More recently, our laboratory has been examining the less well understood mechanism for selective two-electron C–C bond elimination at base-metal centers such as cobalt.³ The rare, selective ethane elimination reactivity of *cis,mer*-(PMe₃)₃Co(CH₃)₂I (**1**) has been central to our preliminary studies.³ In efforts to further probe the many factors influencing this reaction, a series of cobalt(III) *cis,mer*-(PMe₃)₃Co(CH₃)₂X species has been targeted, including X = SPh (**2**) and X = NCS (**3**). These complexes serendipitously demonstrated an interesting alternative pathway to C–C bond elimination, including C–H bond activation of the phenylthiolate and a rare S-atom transfer from the isothiocyanate. The detailed characterization and reactivity of these two sulfur containing cobalt(III) complexes are presented here.

Experimental section

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, cannula or glovebox techniques. Volatile chemicals were dried with 4 Å molecular sieves and distilled prior to use. All chemicals were purchased from Aldrich, VMR, Strem or Cambridge Isotope Laboratories.

(PMe₃)₃Co(CH₃)₃ and (PMe₃)₃Co(CH₃)₂I were prepared as previously reported.⁴ Solvents were dried and deoxygenated using literature procedures.⁵

¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker DRX 600 and 400 Avance MHz spectrometers. ¹H and ¹³C chemical shifts are referenced to residual solvent signals; ³¹P chemical shifts are referenced to an external standard of H₃PO₄. Spectra were obtained at ambient temperature unless otherwise indicated. Due to strong ³¹P–³¹P coupling for *trans*-PMe₃ ligands, some ¹H signals appear as virtual triplets (vt) and are reported as such with the apparent coupling noted. IR spectra were recorded on a Jasco 4100 FTIR. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ or Atlantic Microlab, Inc., in Norcross, GA. X-ray crystallographic data were collected on a Bruker Smart Apex I diffractometer. Samples were collected in inert oil and quick transfer to a cold gas stream. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic calculations were carried out using SHELXTL. The crystal data for complexes **2**, **3** and **3A** are summarized in Table 1.

Preparation of *cis,mer*-(PMe₃)₃Co(CH₃)₂SPh (**2**)

A 50 mL Schlenk flask was charged with 0.057 g (0.172 mmol) of (PMe₃)₃Co(CH₃)₃ and approximately 10 mL diethyl ether. On a Schlenk line, 1 equiv. (18 μL) of thiophenol was added by microsyringe. The solution was stirred for 30 min at ambient temperature changing color from yellow to dark red. The solvent was removed *in vacuo* to afford 45 mg (62%) **2** as red powder. The material may be recrystallized from pentane at –35 °C to obtain material of analytical purity. Anal. Calcd for C₁₇H₃₈P₃SCo: C 47.88; H 8.98. Found: C 47.67; H 8.84. ¹H NMR (C₆D₆): δ –0.82 (bs, 3H, Co–CH₃), 0.76 (bs, 3H, Co–

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† Electronic supplementary information (ESI) available: Variable temperature NMR spectrum of complex **2**. CCDC 1007027–1007029. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01823k

Table 1 Crystal data for compounds 2, 3 and 3A

Compound	2	3	3A
Formula	C ₁₇ H ₃₈ P ₃ SCo	C ₁₂ H ₃₃ NP ₃ SCo	C ₁₈ H ₄₈ N ₂ P ₄ S ₂ Co ₂
Formula weight	426.40	375.32	598.48
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P1
a (Å)	18.100(1)	8.828(1)	8.212(1)
b (Å)	15.500(1)	13.596(1)	8.603(1)
c (Å)	16.368(1)	15.992(1)	11.443(1)
α (°)	90	90	103.448(5)
β (°)	103.642(2)	91.602(1)	102.311(5)
γ (°)	90	90	105.632(4)
V (Å ³)	4462.2(5)	1918.5(1)	723.5(2)
Z	8	4	2
T (K)	183	183	183
Radiation	Mo Kα 0.71073	Mo Kα 0.71073	Mo Kα 0.71073
2θ _{max} (°)	20.92	29.27	24.41
F (000)	1824	800	284
R ₁	0.0234	0.0209	0.0336
wR ₂ (all data)	0.0580	0.0590	0.0850

CH₃), 1.05 (bs, 27H, P-CH₃), 7.01 (m, 1H, C₆H₅), 7.12 (m, 2H, C₆H₅), 7.79 (m, 2H, C₆H₅). ¹H NMR (0 °C, Tol-*d*₈): δ -0.88 (dt, 11.0 Hz, 6.8 Hz, 3H, Co-CH₃), 0.68 (td, 10.2 Hz, 2.5 Hz, 3H, Co-CH₃), 1.03 (vt, 3.2 Hz, 18H, P-CH₃), 1.03 (d, 6.0 Hz, 9H, P-CH₃), 6.98 (m, 1H, C₆H₅), 7.07 (m, 2H, C₆H₅), 7.71 (m, 2H, C₆H₅). ³¹P NMR (C₆D₆): δ -3.02 (bs, 1P), 5.78 (bs, 2P). ¹³C NMR (C₆D₆): δ -10.77 (Co-CH₃), 2.75 (Co-CH₃), 14.75 (P-CH₃), 17.18 (P-CH₃), 122.13, 127.72, 136.09, 149.72 (Ar).

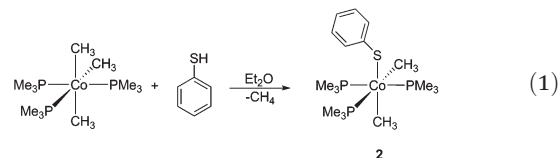
Preparation of *cis,mer*-(PMe₃)₃Co(CH₃)₂NCS (3)

A 20 mL scintillation vial was charged with 0.082 g (0.185 mmol) of (PMe₃)₃Co(CH₃)₂I (1), 0.021 g (0.259 mmol) of NaSCN and approximately 8 mL of THF. The solution was stirred at ambient temperature for 3 h resulting in a color change from orange to yellow. The reaction solution was then transferred to a 25 mL round bottom flask with a vacuum adapter. On a high vacuum line, one equivalent of PMe₃ (0.185 mmol) was added into the mixture at -196 °C *via* calibrated gas bulb. The reaction mixture was then stirred at ambient temperature for 20 min. The volatiles were removed *in vacuo* and the residue was extracted with diethyl ether, filtered through filter paper, concentrated to approximately 3 mL and recrystallized at -35 °C to afford 42 mg (61%) of 3 as a yellow powder. Anal. Calcd for C₁₂H₃₃NP₃SCo: C 38.40; H 8.86; N 3.73. Found: C 38.62; H 8.93; N 3.77. ¹H NMR (C₆D₆): δ -1.24 (dt, 9.9 Hz, 9.3 Hz, 3H, Co-CH₃), 0.36 (td, 10.0 Hz, 3.0 Hz, 3H, Co-CH₃); 0.88 (d, 6.5 Hz, 9H, P-CH₃), 0.91 (vt, 3.3 Hz, 18H, P-CH₃). ³¹P NMR (C₆D₆): δ -1.34 (bs), 13.00 (bs). ¹³C NMR (C₆D₆): δ -15.00 (Co-CH₃), 4.78 (Co-CH₃), 13.59 (P-CH₃), 16.94 (P-CH₃), 139.47 (N=C=S). IR (KBr): ν_{N=C=S} 2091 cm⁻¹.

Results and discussion

Complex 2 was prepared by protonation of (PMe₃)₃Co(CH₃)₃ in diethyl ether using 1 equiv. of thiophenol (eqn (1)).^{4a} A color

change from orange to dark red was observed immediately following the thiophenol addition and red crystals of 2 were precipitated in moderate yield from a pentane extraction at -35 °C. Complex 2 was characterized by NMR spectroscopy and combustion analysis as well as X-ray diffraction. The ¹H NMR spectrum of 2 in benzene-*d*₆ displays features similar to the iodide congener, 1, with two distinct cobalt-methyl resonances at 0.76 and -0.82 ppm.⁶ Both cobalt-methyl peaks are broad at ambient temperature due to rapid intramolecular site exchange.³ At 0 °C, the cobalt-methyl signals resolve into a triplet of doublets and doublet of triplets, consistent with coupling to three ³¹P nuclei (see Fig. S1†). The X-ray diffraction study confirmed the molecular structure of 2. A depiction of one of two molecules of complex 2 found in the asymmetric unit is shown in Fig. 1. The metrical parameters of the two molecules are nearly identical. Complex 2, which has an octahedral geometry with phenylthiolate ligand bound *trans* to one of the cobalt-methyl bonds, is similar in structure to previous reported *cis,mer*-(PMe₃)₃Co(CH₃)₂X congeners.^{4b,6} The strong *trans* influence of the methyl ligand does lead to a slightly longer Co(1)-P(2) distance of 2.254(1) Å in comparison with the Co(1)-P(1) and Co(1)-P(3) distances of 2.226(1) and 2.219(1) Å.



Unlike 1, the phenylthiolate complex 2 afforded competitive ethane elimination and cyclometallation products during thermolysis at 50 °C in benzene-*d*₆ (Fig. 2).

Each reaction pathway likely initiates from trimethylphosphine dissociation at the position *trans* to a methyl group to form a five-coordinate intermediate, which has been implicated in a range of other reactions.^{1b,d,3,7} Following C-C bond

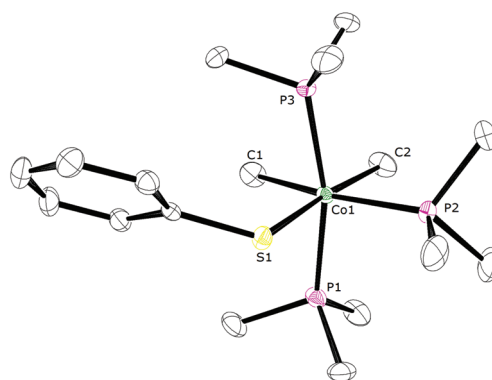


Fig. 1 Molecular structure of 2 at 30% probability ellipsoids. All hydrogen atoms and a second molecule in the asymmetric unit are omitted for clarity. Select bond distances (Å) and angles (°): Co(1)-C(1) 2.033(3), Co(1)-C(2) 2.033(3), Co(1)-P(1) 2.226(1), Co(1)-P(2) 2.254(1), Co(1)-P(3) 2.219(1), Co(1)-S(1) 2.356(1), C(1)-Co(1)-P(2) 167.47(9), C(2)-Co(1)-S(1) 173.4(1), P(1)-Co(1)-P(3) 165.85(3).

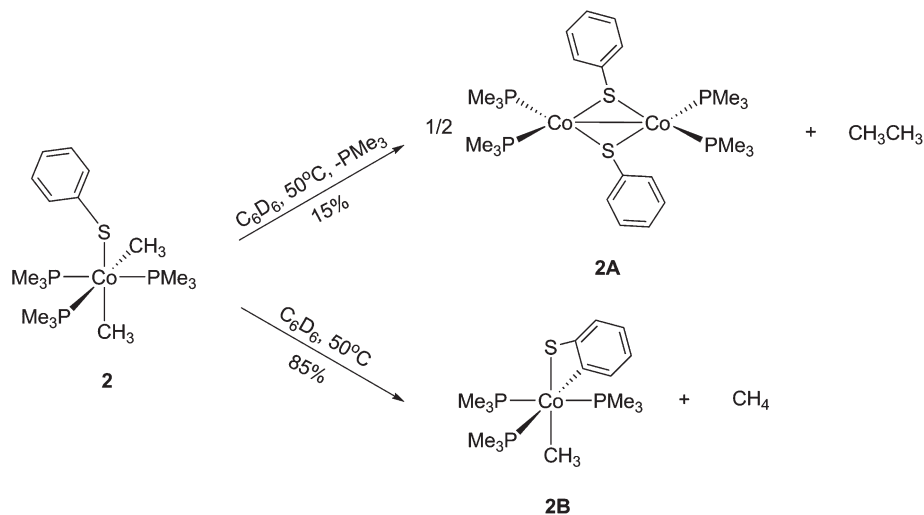
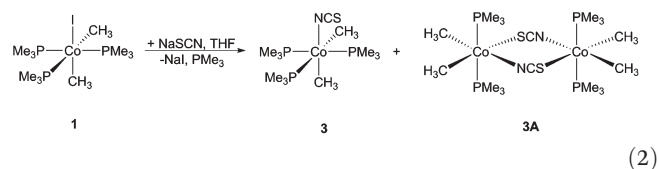


Fig. 2 Thermolysis of complex 2.

coupling to generate ethane, two $(\text{PMe}_3)_2\text{CoSPh}$ moieties bridge the thiolate ligands to form a dinuclear complex **2A**, similar to the observations of Li and co-workers (Fig. 2).⁸ Interestingly, the presence of a phenyl substituent in proximity to the cobalt in **2** also creates an alternative cyclometallation route for the reaction. Given access to the same five-coordinate intermediate proposed for reductive elimination, the close contact of the *ortho* C–H bond and the ability to extrude methane from a cobalt–methyl ligand, cyclometallation becomes a highly favorable process. The sequence of reactions that eliminate methane, be it C–H bond oxidative addition to a transient cobalt(v) species or a σ -bond metathesis/protonation transition structure,⁹ is not discernable with the observations in hand.¹⁰ Notably, when **2-*d*₅** is heated, the degree of cyclometallation was reduced, comprising only 60% of the cobalt products. The identity of the cyclometallation product, **2B** (Fig. 2) may be firmly established by solution spectroscopy, and analogy to a previous report from Beck and co-workers observed this complex from a C–S bond cleavage reaction.¹¹ The ^1H NMR spectrum of complex **2B** in benzene-*d*₆ shows a Co–CH₃ signal at -0.74 ppm as a doublet of triplets and two PMe_3 peaks.¹¹ Though the dual reaction pathways from **2** complicated efforts to study C–C bond elimination, the C–H bond activation reaction observed is nevertheless intriguing given its analogy to several highly studied reactions on platinum with relevance to methane and other C–H bond activations.^{7h,12}

In addition to the protonolysis pathways our laboratory has often employed to obtain congeners of **1**, salt elimination reactions have also proven to be a useful synthetic method. During preliminary investigations, NaSCN was one of several alkali metal salts which successfully replaced the iodide ligand of **1**. However, NMR spectroscopy revealed that more than one product was obtained. Analysis of the NMR spectra as well as the X-ray diffraction data suggested formation of a mononuclear *cis,mer*-(PMe_3)₃Co(CH₃)₂NCS (**3**) as the major product and a minor dimeric analogue **3A** resulting from PMe_3 loss

(eqn (2)).¹³ A few crystals of **3A** were isolated from the mixture permitting X-ray determination of its structure (Fig. 3) which was consistent with the observed ^1H NMR spectrum. The NMR spectrum displays a virtual triplet at 1.24 ppm and two multiplets at -0.13 and -0.56 ppm, respectively, with an integration ratio of 18 : 3 : 3.



Additional evidence for the identity of **3A** came from treatment of the mixture with PMe_3 which led to exclusive conver-

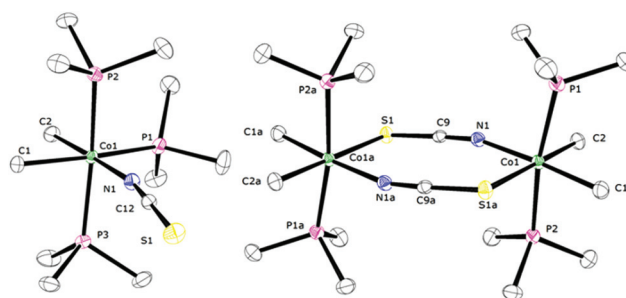
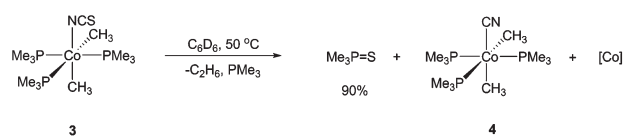


Fig. 3 Molecular structure of **3** (left) and **3A** (right) at 30% probability ellipsoids. All hydrogen atoms are omitted for clarity. Select bond distance (Å) and angles (°). Complex **3**: Co(1)–C(1) 2.037(1), Co(1)–C(2) 2.017(1), Co(1)–P(1) 2.248(1), Co(1)–P(2) 2.234(1), Co(1)–P(3) 2.229(1), Co(1)–N(1) 1.970(1), C(12)–N(1) 1.162(2), C(12)–S(1) 1.639(1), C(1)–Co(1)–P(1) 168.89(4), C(2)–Co(1)–N(1) 177.24(5), P(2)–Co(1)–P(3) 165.18(2), Co(1)–N(1)–C(12) 168.2(1), N(1)–C(12)–S(1) 179.2(1). Complex **3A**: Co(1)–C(1) 1.997(4), Co(1)–C(2) 2.019(3), Co(1)–P(1) 2.216(1), Co(1)–P(2) 2.221(1), Co(1)–N(1) 1.952(3), Co(1)–S(1a) 2.416(1), C(9)–N(1) 1.163(4), C(9)–S(1) 1.647(4), C(1)–Co(1)–N(1) 175.9(1), C(2)–Co(1)–S(1a) 179.77(9), P(1)–Co(1)–P(2) 171.01(4), Co(1)–N(1)–C(9) 164.6(2), N(1)–C(9)–S(1) 176.8(3), C(9)–S(1)–Co(1a) 102.9(1).

sion to **3**. Notably, **3A** did not reappear following removal of the free PMe_3 even at elevated temperature. This suggested **3A** was created by a deficiency of PMe_3 during the synthesis. Indeed, *in situ* NMR experiments confirmed the formation of small amounts of SPMe_3 during the reaction (*vide infra*). The ^1H NMR spectrum of **3** in benzene- d_6 also displays two distinct cobalt–methyl resonances at 0.36 and -1.24 ppm. The molecular structure of complex **3** (Fig. 3) also shows comparable bond distances and angles to its congeners.^{6,4b} The Co(1)–N(1) distance of 1.970(1) Å is slightly longer than a typical Co(III)–NCS bond, probably due to the strong *trans* influence of the methyl ligand.^{14,15} The bond distances of C(12)–N(1) and C(12)–S(1) of 1.162(2) and 1.639(1) Å are typical of cobalt isothiocyanate species reported in the literature.¹⁴

With pure complex **3** in hand, its reactivity under thermolysis was also investigated. After 3 h at 50 °C in benzene- d_6 , a small amount of black precipitate was observed along with formation of ethane and a new doublet located at 1.02 ppm in ^1H NMR spectrum and a singlet at 28.4 ppm in ^{31}P NMR spectrum. Continued heating at 50 °C for 72 h brought this reaction to completion. Collection of the volatile materials and analysis by NMR spectroscopy and GC-MS analysis revealed a nearly 90% conversion (based on Co) to trimethylphosphine sulfide, resulting from a rare S-atom transfer from isothiocyanate (eqn (3)).¹⁶ The non-volatile materials proved to be mostly insoluble even in halogenated solvent; however, limited quantities of *cis,mer*-(PMe_3)₃Co(CH_3)₂(CN) (**4**)^{6a} were detected in ^1H NMR spectrum, consistent with a net S-atom transfer from –NCS. While the poor selectivity between C–C bond elimination and alternative reaction pathways for **3** is not ideal for further experimental mechanistic study, the S-atom transfer reaction of the isothiocyanate is one with little precedent and is possible interest for oxidative sulfur additions.^{16a,b,d}



(3)

Conclusion

In summary, two cobalt(III) *cis,mer*-(PMe_3)₃Co(CH_3)₂X species (X = SPh, NCS) were prepared *via* protonolysis and salt elimination methods. Each complex showed unique reactivity upon thermolysis in benzene giving combinations of C–C bond reductive elimination, arene *ortho*-C–H bond activation, and S-atom transfer chemistry. The phenylthiolate species provided an unusual example of C–H bond cyclometallation from such a ligand at a first row transition metal. S-atom transfer from the isothiocyanate congener appears to be a quite rare example of a metal bound –NCS ligand acting as an efficient S-atom donor. Such reactivity could be of interest in endeavors to apply first row transition metals to synthetic methods for oxidative sulfur transfer.

Acknowledgements

We gratefully acknowledge funding by the National Science Foundation (CHE-1350047) and the American Chemical Society Petroleum Research Fund (52066-DNI3).

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