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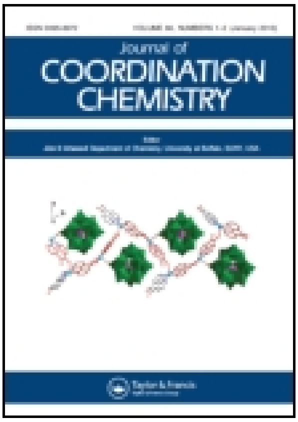

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Synthesis and structural characterization of dicobalt-iron clusters containing bridging diphosphine ligands

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Synthesis and structural characterization of dicobalt–iron clusters containing bridging diphosphine ligands

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Reaction of (μ_3-S)$FeCo_2(CO)_9$ with N-substituted bis(diphenylphosphanyl)amine $Ph_2PN(R)PPh_2$ ($R = CH_2CH_2CH_3$, **A**; CH_2Ph, **B**) at room temperature in CH_2Cl_2 afforded dicobalt–iron cluster complexes (μ_3-S)$FeCo_2(CO)_7[Ph_2PN(R)PPh_2]$ ($R = CH_2CH_2CH_3$, **1**; CH_2Ph, **2**) in 75% and 66% yields, respectively. **1** and **2** were characterized by elemental analysis and spectroscopy. In addition, the molecular structures of **A**, **1**, and **2** were determined by single crystal X-ray diffraction analysis.

Keywords: Dicobalt–iron; Cluster complex; Diphosphine ligand; Synthesis; Crystal structure

1. Introduction

Mixed-metal clusters can be used as catalysts in a variety of reactions [1]. The dicobalt–iron cluster (μ_3-S)$FeCo_2(CO)_9$ can be prepared by reaction of $Fe(CO)_5$, $Co_2(CO)_8$ and thiophene or ethanethiol [2], or by reaction of (μ-S_2)$Fe_2(CO)_6$ with $Co_2(CO)_8$ [2, 3]. Monosubstituted or disubstituted derivatives, for example, (μ_3-S)$FeCo_2(CO)_8[P(OCH_2Ph)_3]$ [4], (μ_3-S)$FeCo_2(CO)_7$(bpcd) (bpcd = 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione) [5], (μ_3-S)$FeCo_2(CO)_7$(dppfe) (dppfe = $Ph_2PC_5H_4FeC_5H_4PPh_2$) [6] and (μ_3-S)$FeCo_2(CO)_7(O[P(SCH_2)_2]_2)$ [7], were obtained from reactions of (μ_3-S)$FeCo_2(CO)_9$ with monophosphine or diphosphine ligands. To extend study on clusters, we carried out reactions of (μ_3-S)$FeCo_2(CO)_9$ with bidentate *N*,*N*-bis(diphenylphosphanyl)amine $Ph_2PN(R)PPh_2$ ($R = CH_2CH_2CH_3$, CH_2Ph) and have prepared (μ_3-S)$FeCo_2(CO)_7[Ph_2PN(R)PPh_2]$ ($R = CH_2CH_2CH_3$, CH_2Ph) with bridging diphosphine ligands. Herein, we report our results.

2. Experimental

2.1. *Materials and methods*

All reactions were performed using standard Schlenk and vacuum-line techniques under N_2. CH_2Cl_2 was distilled over CaH_2 under N_2. (μ_3-S)$FeCo_2(CO)_9$ [2] and $Ph_2PN(R)PPh_2$ ($R = CH_2CH_2CH_3$, CH_2Ph) [8] were prepared according to literature procedures. IR spectra

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were recorded on a Nicolet MAGNA 560 FTIR spectrometer. ^{1}H (^{31}P, ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer at room temperature. Elemental analyses were performed by a Perkin-Elmer 240C analyzer, while ESI-MS data were obtained on a Bruker Micro TOF Q-II instrument.

2.2. Synthesis of (μ_3-S)FeCo$_2$(CO)$_7$[Ph$_2$PN(CH$_2$CH$_2$CH$_3$)PPh$_2$] (1)

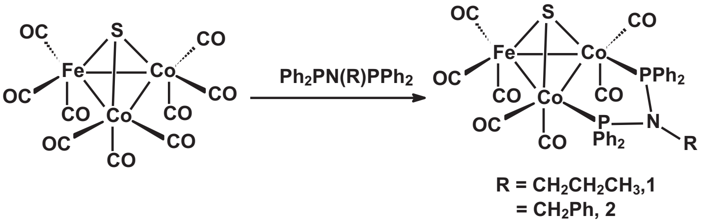
A solution of (μ_3-S)FeCo$_2$(CO)$_9$ (0.092 g, 0.2 mmol) and Ph$_2$PN(CH$_2$CH$_2$CH$_3$)PPh$_2$ (0.085 g, 0.2 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at room temperature overnight. The solvent was reduced *in vacuo,* and the residue was subjected to TLC separation using CH$_2$Cl$_2$/petroleum ether (v/v = 1:5) as eluent. Collecting the main brown band afforded 0.125 g (75%) of **1** as a black solid. Anal. Calcd for $C_{34}H_{27}Co_2FeNO_7P_2S$: C, 49.24%; H, 3.28%; N, 1.69%. Found: C, 49.52%; H, 3.34%; N, 1.60%. IR (KBr disk): $\nu_{C\equiv O}$ 2051 (vs), 2012 (vs), 1992 (vs), 1935 (vs) cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74–7.66 (m, 8H, Ph*H*), 7.56 (s, 12H, Ph*H*), 2.54 (quintet, $J = 8$ Hz, 2H, NC*H*$_2$), 0.46 (sextet, 2H, NCH$_2$C*H*$_2$), 0.12 (t, $J = 7$ Hz, 3H, C*H*$_3$) ppm. ^{31}P NMR (200 MHz, CDCl$_3$, 85% H$_3$PO$_4$): δ 103.19 (s) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 213.59 (*C*≡O), 136.62, 136.30, 136.26, 135.93, 132.30, 132.20, 131.55, 131.45, 130.83, 128.80, 128.76, 128.72, 128.51, 128.48, 128.44 (Ph*C*), 54.40 (N*C*H$_2$), 23.09 (NCH$_2$*C*H$_2$), 10.75 (*C*H$_3$) ppm. ESI-MS: *m/z* 828.6 [M^{+}].

Table 1. Crystal data and structure refinement details for **A**, **1** and **2**.

Compound	**A**	**1**·0.13CH$_2$Cl$_2$	**2**
Empirical formula	$C_{27}H_{27}NP_2$	$C_{34.13}H_{27.25}Cl_{0.25}Co_2FeNO_7P_2S$	$C_{38}H_{27}Co_2FeNO_7P_2S$
Formula weight	427.44	839.89	877.32
Temperature (K)	113(2)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)	$P\bar{1}$	$P\bar{1}$
a (Å)	10.5636(12)	10.980(3)	11.5121(19)
b (Å)	9.5884(10)	17.691(4)	12.514(3)
c (Å)	23.561(2)	18.951(4)	14.744(4)
α (°)	90	96.621(3)	78.113(15)
β (°)	101.784(4)	92.439(3)	69.916(15)
γ (°)	90	105.453(4)	65.777(14)
V (Å^3)	2336.1(4)	3514.2(14)	1814.1(7)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.215	1.587	1.606
μ (mm^{-1})	0.200	1.558	1.495
F(000)	904	1701	888
Crystal size (mm^3)	0.20 × 0.20 × 0.10	0.20 × 0.18 × 0.10	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	1.77, 27.86	1.72, 27.91	1.47, 27.90
Reflections collected/unique	24,523/9818	37,157/16,538	19,181/8550
R_{int}	0.0658	0.0584	0.0366
h k l range	$-13 \leqslant h \leqslant 12$ $-9 \leqslant k \leqslant 12$ $-30 \leqslant l \leqslant 30$	$-14 \leqslant h \leqslant 12$ $-21 \leqslant k \leqslant 23$ $-24 \leqslant l \leqslant 24$	$-15 \leqslant h \leqslant 13$ $-16 \leqslant k \leqslant 16$ $-19 \leqslant l \leqslant 19$
Completeness to θ_{max} (%)	99.6	98.3	98.5
Data/restraints/parameters	9818/1/543	16,538/20/894	8550/0/469
Goodness of fit on F^2	0.976	1.025	1.071
$R1/wR2$ ($I > 2\sigma(I)$)	0.0486/0.0817	0.0493/0.0979	0.0264/0.0769
$R1/wR2$ (all data)	0.0582/0.0855	0.0661/0.1055	0.0769/0.0789
Largest diff. peak and hole/eÅ^{-3}	0.347/−0.372	1.370/−0.684	0.436/−0.481

2.3. *Synthesis of (μ_3-S)FeCo$_2$(CO)$_7$[Ph$_2$PN(CH$_2$Ph)PPh$_2$] (2)*

The procedure was similar to that of **1** except $Ph_2PN(CH_2Ph)PPh_2$ (0.095 g, 0.2 mmol) was used instead of $Ph_2PN(CH_2CH_2CH_3)PPh_2$. 0.115 g (66%) of **2** was obtained as a black solid. Anal. Calcd for $C_{38}H_{27}Co_2FeNO_7P_2S$: C, 52.02%; H, 3.10%; N, 1.60%. Found: C, 51.82%; H, 3.34%; N, 1.72%. IR (KBr disk): $\nu_{C\equiv O}$ 2050 (vs), 2005 (vs), 1991 (vs), 1928 (vs) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (s, 4H, Ph*H*), 7.66 (s, 4H, Ph*H*), 7.52 (s, 6H, Ph*H*), 7.45, 7.43 (2s, 6H, Ph*H*), 6.85 (t, *J* = 7 Hz, 1H, Ph*H*), 6.69 (t, *J* = 7.5 Hz, 2H, Ph*H*), 5.84 (d, *J* = 8 Hz, 2H, Ph*H*), 4.07 (t, *J* = 7 Hz, 2H, C*H*$_2$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): δ 107.31 (s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.57 (*C*≡O), 136.32, 135.97, 135.64, 135.26, 133.12, 133.07, 133.02, 131.84, 131.79, 131.74, 130.74, 130.65, 128.68, 128.61, 128.32, 128.28, 128.24, 127.38, 127.20 (Ph*C*), 55.44 (*C*H$_2$) ppm. ESI-MS: *m/z* 876.6 [M$^+$].



Scheme 1. Preparation of **1** and **2**.

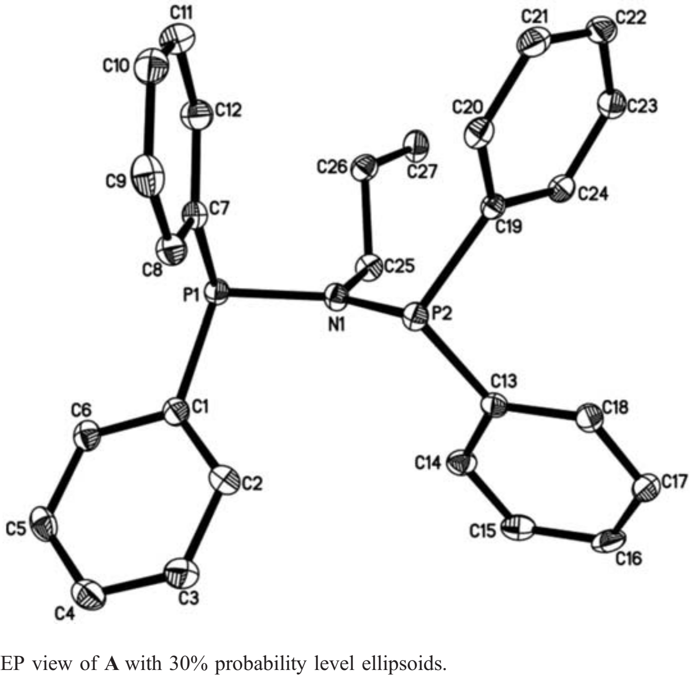


Figure 1. ORTEP view of **A** with 30% probability level ellipsoids.

2.4. *X-ray structure determination*

Single crystals of **A**, **1,** and **2** suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/ethanol solution of **A** and CH_2Cl_2/hexane solutions of **1** and **2** at 4 °C. A single crystal of **A**, **1,** or **2** was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω-ϕ scanning mode. Data collection, reduction, and absorption correction were performed by *CRYSTALCLEAR* [9]. The structure was solved by direct methods using SHELXS-97 [10] and refined by full-matrix least-squares techniques (SHELXL-97) [11] on F^2. Hydrogens were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

3. Results and discussion

3.1. *Synthesis and characterization*

Reaction of (μ_3-S)$FeCo_2(CO)_9$ with 1 equiv of *N*-substituted bis(diphenylphosphanyl)amine $Ph_2PN(R)PPh_2$ ($R = CH_2CH_2CH_3$, **A**; CH_2Ph, **B**) at room temperature in CH_2Cl_2 gave dicobalt–iron cluster complexes **1** and **2** in 75% and 66% yields, respectively (Scheme 1).

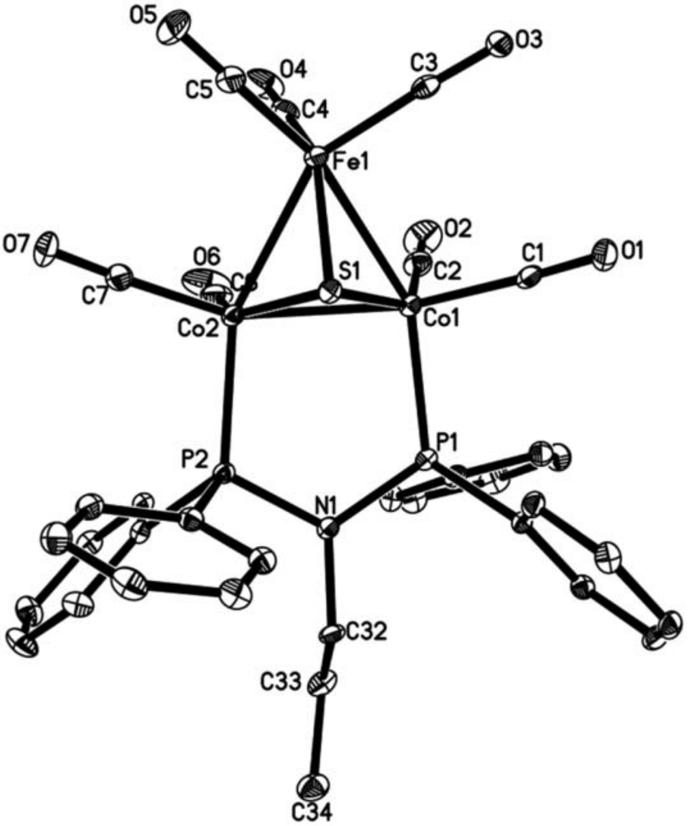


Figure 2. ORTEP view of **1** with 30% probability level ellipsoids.

The new complexes **1** and **2** are air-stable black solids, characterized by elemental analysis and spectroscopy. IR spectra of **1** and **2** show four absorptions at 2051 – 1928 cm^{-1} for their terminal carbonyls and the $\nu_{C\equiv O}$ values markedly shifted to lower frequencies relative to (μ_3-S)$FeCo_2(CO)_9$ (2106, 2067, 2054, 2041, 2029, 1973 cm^{-1}) [3]. The ^{31}P NMR spectra of **1** and **2** display a singlet at δ 103.19 and 107.31 ppm, respectively, indicating that both phosphorus of the bidentate ligand coordinate to two cobalts of the $FeCo_2$ cluster. The ^{13}C NMR spectra of **1** and **2** exhibit a singlet at δ 213.5 ppm for their terminal carbonyls.

3.2. *X-ray crystal structures*

The molecular structures of **A**, **1,** and **2** have been confirmed by single crystal X-ray diffraction analysis. ORTEP views of **A**, **1**, and **2** are shown in figures 1–3 and selected bond lengths and angles are given in Table 2. The known compound **A** crystallizes in the monoclinic space group $P2_1$. The unit cell contains two molecules of $Ph_2PN(CH_2CH_2CH_3)PPh_2$. As shown in figure 1, the diphenylphosphanyl groups are staggered relative to the PNP backbone. The angles around nitrogen are 120.85(17)°, 114.98(17)°, and 123.13(11)°, indicating that it exhibits a distorted trigonal-pyramidal geometry. The crystal structure of **A** is consistent with previously reported N-substituted bis(diphenylphosphanyl)amine of the type $Ph_2PN(R)PPh_2$ [8, 12, 13].

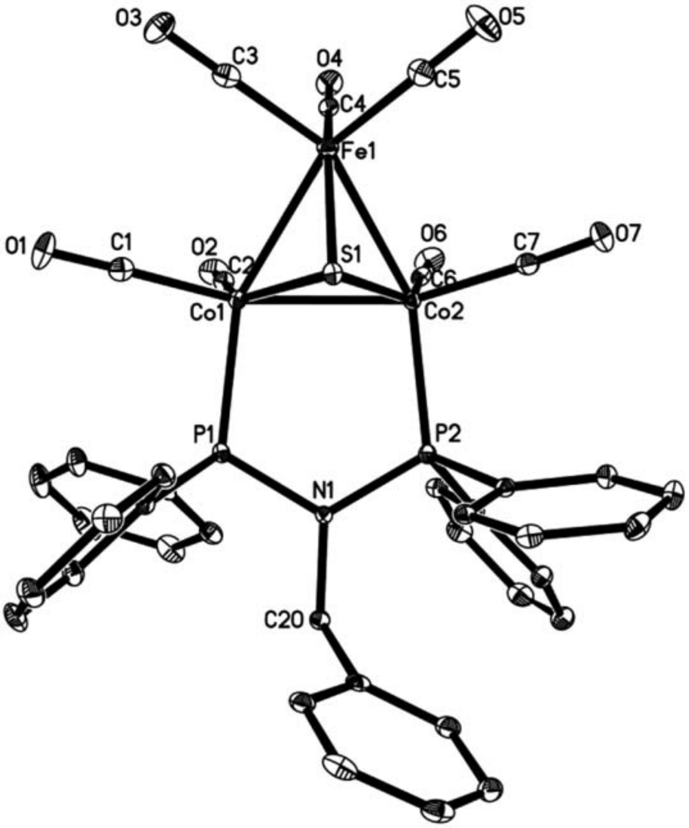


Figure 3. ORTEP view of **2** with 30% probability level ellipsoids.

Table 2. Selected bond lengths (Å) and angles (°) for **A**, **1** and **2**.

A			
P(1)–N(1)	1.723(2)	P(2)–N(1)	1.718(2)
P(1)–C(1)	1.848(3)	P(2)–C(13)	1.841(3)
C(25)–N(1)–P(2)	120.85(17)	C(25)–N(1)–P(1)	114.98(17)
P(2)–N(1)–P(1)	123.13(11)	N(1)–P(1)–C(7)	103.38(11)
1			
Co(1)–S(1)	2.1596(10)	Co(1)–P(1)	2.2079(10)
Co(1)–Co(2)	2.4885(8)	Co(1)–Fe(1)	2.5263(7)
Co(2)–S(1)	2.1716(9)	Co(2)–P(2)	2.1964(10)
Co(2)–Fe(1)	2.5273(7)	Fe(1)–S(1)	2.1776(10)
P(1)–N(1)	1.713(3)	P(2)–N(1)	1.700(2)
S(1)–Co(1)–Co(2)	55.16(3)	S(1)–Co(1)–Fe(1)	54.71(3)
P(1)–Co(1)–Co(2)	93.74(3)	Co(2)–Co(1)–Fe(1)	60.521(17)
P(1)–Co(1)–Fe(1)	153.20(3)	S(1)–Co(2)–Co(1)	54.71(2)
P(2)–Co(2)–Co(1)	96.63(3)	S(1)–Co(2)–Fe(1)	54.58(3)
P(2)–Co(2)–Fe(1)	149.64(3)	Co(1)–Co(2)–Fe(1)	60.479(19)
Co(1)–Fe(1)–Co(2)	59.00(2)	P(2)–N(1)–P(1)	118.33(15)
2			
Co(1)–S(1)	2.1648(9)	Co(1)–P(1)	2.1933(8)
Co(1)–Co(2)	2.4889(6)	Co(1)–Fe(1)	2.5363(8)
Co(2)–S(1)	2.1783(8)	Co(2)–P(2)	2.2136(8)
Co(2)–Fe(1)	2.5361(6)	Fe(1)–S(1)	2.1726(8)
P(1)–N(1)	1.7079(18)	P(2)–N(1)	1.7184(19)
S(1)–Co(1)–Co(2)	55.29(2)	S(1)–Co(1)–Fe(1)	54.36(2)
P(1)–Co(1)–Co(2)	96.07(3)	Co(2)–Co(1)–Fe(1)	60.610(18)
P(1)–Co(1)–Fe(1)	152.48(2)	S(1)–Co(2)–Co(1)	54.78(2)
P(2)–Co(2)–Co(1)	95.53(3)	S(1)–Co(2)–Fe(1)	54.24(2)
P(2)–Co(2)–Fe(1)	150.63(2)	Co(1)–Co(2)–Fe(1)	60.62(2)
Co(1)–Fe(1)–Co(2)	58.770(19)	P(2)–N(1)–P(1)	117.94(10)

Both **1** and **2** crystallize in triclinic space group *P*-1. The unit cell of **1** contains two molecules of (μ_3-S)FeCo$_2$(CO)$_7$[Ph$_2$PN(CH$_2$CH$_2$CH$_3$)PPh$_2$] and one molecule of CH$_2$Cl$_2$, whereas **2** has one molecule of (μ_3-S)FeCo$_2$(CO)$_7$[Ph$_2$PN(CH$_2$Ph)PPh$_2$]. Complexes **1** and **2** (figures 2 and 3) both contain a dicobalt–iron triangle cluster capped by a μ_3-S ligand with seven carbonyls and one bridging Ph$_2$PN(R)PPh$_2$ (R = CH$_2$CH$_2$CH$_3$ or CH$_2$Ph). Phosphorus of bidentate phosphine resides in apical position of cobalt, close to the crystal structure of [Co$_2$Fe(μ_3-S){μ-PPh$_2$C(SMe)=S}(CO)$_8$] [14] and [Co$_2$Fe(μ_3-S){μ-cyclo-(PhP)$_6$}(CO)$_7$] [15]. The average M-M bond lengths (2.5140 Å for **1** and 2.5204 Å for **2**) are slightly shorter than that of (μ_3-S)FeCo$_2$(CO)$_9$ (2.557 Å) [16], whereas the average M–S bond lengths (2.1696 Å for **1** and 2.1759 Å for **2**) are slightly longer than the corresponding average M–S distance (2.158 Å) in (μ_3-S)FeCo$_2$(CO)$_9$ [16]. These differences can be attributed to the carbonyl substitution by the bidentate phosphine.

4. Conclusions

Carbonyl substitution of (μ_3-S)FeCo$_2$(CO)$_9$ with N-substituted bis(diphenylphosphanyl) amine Ph$_2$PN(R)PPh$_2$ (R = CH$_2$CH$_2$CH$_3$, CH$_2$Ph) gave mixed-metal dicobalt–iron clusters with bridging diphosphine ligands. The new complexes were characterized by elemental analysis, NMR and IR spectroscopy and the molecular structures of **A**, **1**, and **2** were determined by single-crystal X-ray diffraction analysis. These complexes have potential applications in catalysis and further studies are in progress in our laboratory.

Supplementary material

CCDC 901,591 (**A**), 902,265 (**1**) and 902,264 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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References

[1] P. Braunstein, J. Rosé. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, R.D. Adams, F.A. Cotton (Eds.), Chap. 13, Wiley-VCH, New York, NY (1998).
[2] S.A. Khattab, L. Marko, G. Bor, B. Marko. *J. Organomet. Chem.*, **1**, 373 (1964).
[3] M. Cowie, R.L. Dekock, T.R. Wagenmaker, D. Seyferth, R.S. Henderson, M.K. Gallagher. *Organometallics*, **8**, 119 (1989).
[4] X.-L. Wang, Q.-L. Suo, Y.-B. Wang, Q.-W. Chinese. *Chinese J. Struct. Chem.*, **17**, 97 (1998).
[5] S.G. Bott, J. Wang, H. Shen, M.G. Richmond. *J. Chem. Crystallogr.*, **29**, 391 (1999).
[6] H. Zhang, Q.-L. Suo, Y.-B. Wang, L. Wang, L.-H. Weng, X.-B. Leng. *Acta Phys. Chim. Sin.*, **18**, 746 (2002).
[7] X. Wang, Q. Suo, Y. Wang. *Acta Phys. Chim. Sin*., **15**, 757 (1999).
[8] X.-F. Liu, W.-H. Xu, H. Li. *Acta Crystallogr.*, **E67**, 370 (2011).
[9] *CRYSTALCLEAR 1.3.6*. Rigaku and Rigaku/MSC, The Woodlands, TX (2005).
[10] G.M. Sheldrick. *SHELXS97, A Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
[11] G.M. Sheldrick. *SHELXL97, A Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[12] T. Mayer, H.C. Böttcher. *Z. Naturforsch.*, **67b**, 504 (2012).
[13] T. Mayer, H.C. Böttcher. *J. Organomet. Chem.*, **715**, 64 (2012).
[14] J.D. King, M.J. Mays, C.-Y. Mo, G.A. Solan, G. Conole, M. McPartlin. *J. Organomet. Chem.*, **642**, 227 (2002).
[15] R.M. De Silva, M.J. Mays, P.R. Raithby, G.A. Solan. *J. Organomet. Chem.*, **642**, 237 (2002).
[16] D.L. Stevenson, C.H. Wei, L.F. Dahl. *J. Am. Chem. Soc.*, **93**, 6027 (1971).