© 2004 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 77, 103–107 (2004) 103

Synthesis of Mono- and Tri-Nuclear Ruthenium Carbonyl Complexes Containing the Pyridine-2-thiolato Ligand and Reactivity of a Bis(pyridine-2-thiolato) Chelated Ruthenium Dicarbonyl Complex with a Novel Cobalt-Containing Diphosphine Ligand

Fung-E Hong,* Yu-Chang Chang, and Shu-Chun Chen

Department of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan

Received March 27, 2003; E-mail: fehong@dragon.nchu.edu.tw

The reaction of 3-cyano-4,6-dimethyl-pyridine-2-thiol with $Ru_3(CO)_{12}$ in toluene at 55 °C for 20 h gave three complexes: $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **5**, $[Ru(4,6\text{-CH}_3\text{-3-CN-py-}\kappa N\text{-thiol-}\kappa S)_2(CO)_2]$ **7** and presumably $[Ru_3(CO)_9(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **6**. The deprotonated mercaptopyridine acts either as a bridging ligand in **5** and **6** or as a chelating ligand in **7**. Further reaction of **7** with a novel cobalt-containing diphosphine ligand, $[Co_2(CO)_4\{\mu\text{-PPh}_2CH_2PPh_2\}\{\mu\text{-PPh}_2C{\equiv}CPPh_2\}]$ **8**,[1] probably resulted in the formation of probably a **8**-chelated complex, $[Ru(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})(4,6\text{-CH}_3\text{-3-CN-2-S-py-}\kappa S)(PPh_2CH_2PPh_2)(\{\mu\text{-PPh}_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-PPh}_2C{\equiv}CPPh_2\})]$ **10**. All the compounds were characterized by spectroscopic means; furthermore, compounds **5** and **7** were studied by X-ray diffraction methods.

Studies of the structure and reactivity of various sulfido–metallic clusters have provided valuable information for the understanding of heterogeneous metal-catalyzed hydrodesulfurization.[2] Our previous works had demonstrated a general route of preparing pyridyl derivatives bridging sulfido tricobalt carbonyl clusters, **2**- and **3**-like, from the reactions of a variety of pyridinethiols with $Co_2(CO)_8$ (Scheme 1). Obviously, the S–H and C–S bonds of the pyridinethiol were ruptured during the formation of products. In some cases, tris(pyridinethiolato) chelated monocobalt complexes, **4**-like, were observed as well.[3]

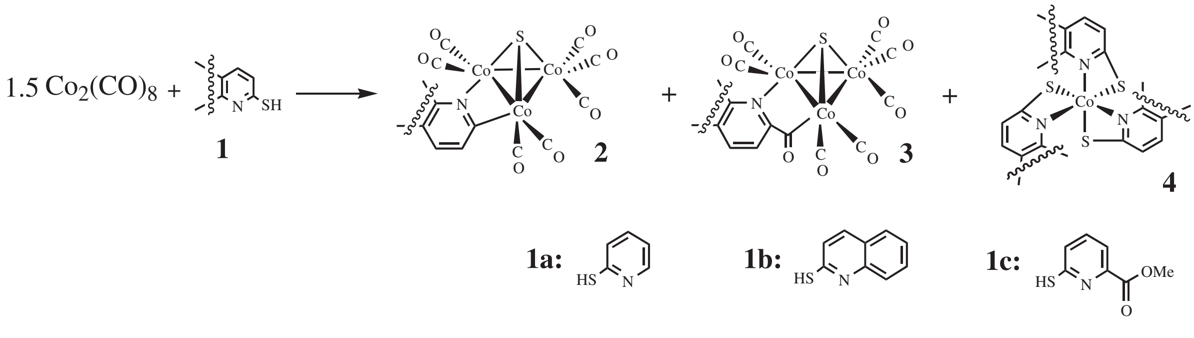
Only a few attempts have so far been made at preparing sulfidotriruthenium carbonyl clusters. The preparation of sulfidotriruthenium carbonyl cluster, $[(\mu\text{-H})_2(\mu_3\text{-S})Ru_3(CO)_9]$, reported previously was through the direct reaction of H_2S with $Ru_3(CO)_{12}$.[4] Further oxidative treatment of this compound with $SnCl_4$ was also studied.[5] Other early accounts on the formation of sulfidotriruthenium carbonyl clusters were through the reaction of pyridinethiol or mercaptoethanoic acid with $Ru_3(CO)_{12}$.[6] Unlike the sulfidotricobalt cluster, the deprotonated pyridinethiol bonds to the triruthenium carbonyl cluster through a bridging sulfur (μ_2-SR) and a coordinating pyridyl.

We should like to explore a further possibility of forming sulfidotriruthenium carbonyl clusters from the reaction of multi-substituted pyridinethiol with $Ru_3(CO)_{12}$. Here we report the reactions between 3-cyano-4,6-dimethyl-pyridine-2-thiol with $Ru_3(CO)_{12}$ and a further reaction of the produced bis(pyridinethiolato) chelated ruthenium complex with unique organometallic diphosphine ligand, $[Co_2(CO)_4\{\mu\text{-PPh}_2CH_2PPh_2\}\{\mu\text{-PPh}_2C{\equiv}CPPh_2\}]$ **8**.

Results and Discussion

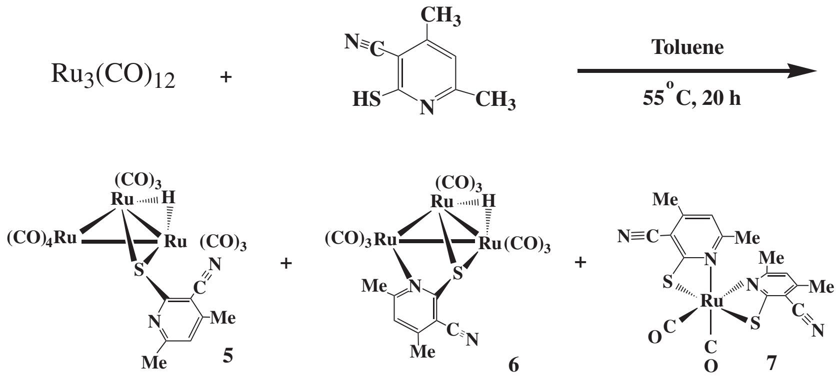
The reaction of 3-cyano-4,6-dimethyl-2-mercaptopyridine with $Ru_3(CO)_{12}$ in toluene at 55 °C for 20 h gave $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **5**, $[Ru(4,6\text{-CH}_3\text{-3-CN-py-}\kappa N\text{-thiol-}\kappa S)_2(CO)_2]$ **7** and presumably $[Ru_3(CO)_9(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **6**[7] (Scheme 2).

Compounds **5** and **7** were well characterized by spectroscopic means as well as X-ray crystal structure determination (Table 1). In ^1H NMR, a signal with chemical shift at −15.6 ppm for **5** indicates the existence of a bridging hydride. Two sets of singlet corresponding to the two methyl groups were ob-



Scheme 1.

Published on the web January 13, 2004; DOI 10.1246/bcsj.77.103



Scheme 2.

Table 1. Crystal Data of **5** and **7**

Compound	**5**	**7**
Formula	$C_{18}H_8N_2O_{10}Ru_3S$	$C_{19}H_{16}Cl_2N_4O_2RuS_2$
Formula weight	747.53	568.45
Cryst syst	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.1249(8)	8.0959(8)
b/Å	10.1739(8)	8.4823(8)
c/Å	12.7472(10)	17.5267(16)
α/°	72.692(2)	81.752(2)
β/°	85.332(2)	81.465(2)
γ/°	74.0580(10)	78.690(2)
V/Å^3	1205.41(16)	1159.00(19)
Z	2	2
D_c/Mg m^{-3}	2.060	1.629
λ(Mo Kα)/Å	0.71073	0.71073
μ/mm^{-1}	1.996	1.110
θ range/deg	2.09 to 26.02	2.37 to 25.98
Observed reflections ($F > 4\sigma(F)$)	4666	4447
No. of refined parameters	311	271
$R1$[a)] for significant reflctns	0.0388	0.0367
$wR2$[b)] for sigft reflctns	0.1107	0.1148
GoF[c)]	0.997	0.940

a) $R1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$. b) $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 0.10$ for **5** and **7**. c) GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{\mathrm{rflns}} - N_{\mathrm{params}})]^{1/2}$.

served. The molecular structure of **5** reveals that it is a thiolato-bridged, hydrido-bridged triruthenium compound (Fig. 1). It can also be regarded as a Ru_3S unit taking a butterfly shape.[8] The thiolate acts as a bridging, three-electron donating ligand. Both the thiolato and hydrido ligand bridge the same diruthenium edge. It comes naturally for the pyridine ring to locate in a less crowded region, which is away from the triruthenium center. The bond lengths of Ru(2)–S and Ru(3)–S are 2.4004(11) Å and 2.3878(11) Å, respectively. They are close to each other. The bond lengths of Ru(1)–Ru(2), Ru(1)–Ru(3) and Ru(2)–Ru(3) are 2.8329(5) Å, 2.8377(6) Å and 2.8494(5) Å, respectively. They are almost equal within the experimental errors. A slow conversion of **5** to **6** was observed in solution. The reverse process did not occur under extra pressure of CO. We also observed the insolubility of **6** in most of the commonly used solvents, such as CH_2Cl_2 or THF. The collection of spectroscopic data for **6** was rather difficult due to its insolubility in solution.[9] A tentative structural assignment for **6**, based on available spectroscopic data, is shown in Scheme 2. Two compounds, **5** and **6**, were produced in almost equal quantity. Interestingly, in a closely related case the **6**-like rather than the **5**-like compound was observed as the major product.[6] It is most likely that the substituents on the pyridyl ring retard the conversion of **5** to **6** through steric hindrance. Contrasting to the sulfidotricobalt clusters shown in Scheme 1, the pyridinethiolato ligand bonds to the triruthenium carbonyl cluster through a bridging sulfido ligand (μ_2-SR). The longer metal–metal bond length of the triruthenium cluster might prevent the bridging of the pryidyl ligand.[10] There is only one set of signals for two chelating bis(pyridinethiolato) ligands of **7** in ^{1}H NMR, which indicates the chemically equivalent nature of these two ligands. This is also evidenced by the fact that only one set of signals was observed for **7** in ^{13}C NMR. The molecular structure of **7** shows that it is a bis(pyridinethiolato) chelated monoruthenium carbonyl complex (Fig. 2). The central metal is in a roughly octahedral environment. Solvent molecules, CH_2Cl_2, were found

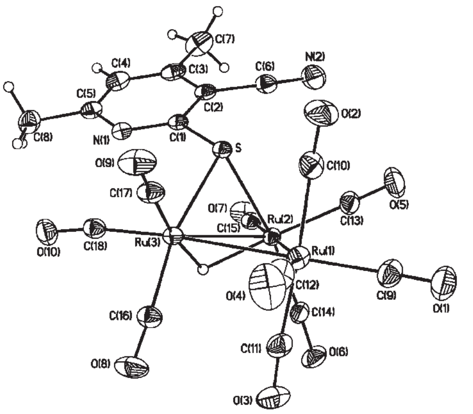


Fig. 1. The molecular structure of $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}4,6\text{-}CH_3\text{-}3\text{-}CN\text{-}2\text{-}S\text{-}py)]$ **5**. Selected bond lengths (Å) and bond angles (°) for **5**: Ru(1)–Ru(2) 2.8329(5), Ru(1)–Ru(3) 2.8377(6), Ru(2)–Ru(3) 2.8494(5), S–Ru(2) 2.4004(11), S–Ru(3) 2.3878(11), Ru(1)–C(11) 1.933(7), Ru(1)–C(12) 1.933(6), Ru(1)–C(9) 1.933(7), Ru(1)–C(10) 1.968(7), Ru(2)–C(14) 1.901(5), Ru(2)–C(13) 1.907(6), Ru(2)–C(15) 1.932(5), Ru(3)–C(16) 1.896(5), Ru(3)–C(17) 1.897(5), Ru(3)–C(18) 1.943(6), Ru(2)–Ru(1)–Ru(3) 60.329(12), Ru(1)–Ru(2)–Ru(3) 59.919(14), Ru(1)–Ru(3)–Ru(2) 59.751(13), S–Ru(2)–Ru(3) 53.28(3), S–Ru(3)–Ru(2) 53.68(3), Ru(2)–S–Ru(3) 73.04(3).

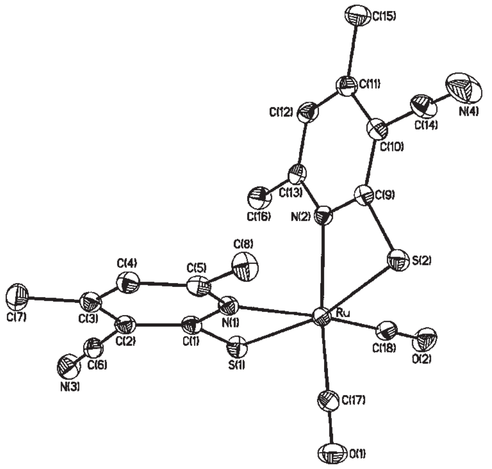


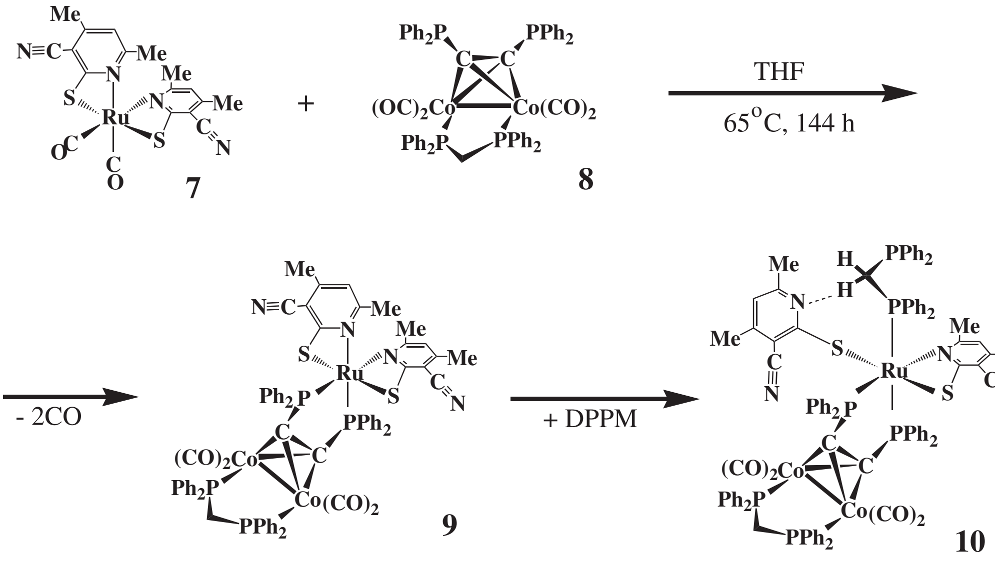
Fig. 2. The molecular structure of $[Ru(4,6\text{-}CH_3\text{-}3\text{-}CN\text{-}py\text{-}\kappa N\text{-}thiol\text{-}\kappa S)_2(CO)_2]$ **7**. Selected bond lengths (Å) and bond angles (°) for **7**: Ru–N(1) 2.172(3), Ru–N(2) 2.192(3), Ru–S(1) 2.4166(9), Ru–S(2) 2.4193(9), Ru–C(17) 1.865(4), Ru–C(18) 1.864(4), S(1)–Ru–C(17) 90.76(11), S(2)–Ru–C(18) 89.66(12), N(1)–Ru–C(17) 89.72(14), N(2)–Ru–C(18) 93.66(13), C(17)–Ru–C(18) 91.11(17).

to be intercalated in the spaces of the packed molecules. Scheme 2 shows that the S–H bond of the pyridine-2-thiol broke after the reaction to yield compound **5**, **6**, or **7**, respectively, in contrast to the reaction in Scheme 1. Moreover, the fact that two coordinated pyridyls take the opposing positions against the carbonyls is suggested through the donating/accepting manner of the two trans-ligands.[11]

Didentate phosphine ligands have become an indispensable part of the transition metal based homogeneous catalysis.[12] A well chosen didentate phosphine ligand is essential for an effective catalytic performance. Our previous work described the preparation of a new type of metal-containing didentate phosphine ligand, $[Co_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}PPh_2C{\equiv}CPPh_2)]$ **8**. It was prepared from the reaction of a bi-functional ligand bis(diphenylphosphino)acetylene (dppa) with one equivalent of a bis(diphenylphosphino)methane (dppm) bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$.[1]

Treatment of **7** with **8** in THF at 65 °C for 144 h gave an unexpected **8**-chelated complex, $[Ru(\mu\text{-}4,6\text{-}CH_3\text{-}3\text{-}CN\text{-}2\text{-}S\text{-}py)(4,6\text{-}CH_3\text{-}3\text{-}CN\text{-}2\text{-}S\text{-}py\text{-}\kappa S)(PPh_2CH_2PPh_2)(\{\mu\text{-}PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-}PPh_2C{\equiv}CPPh_2\})]$ **10** with oxidized **8**. (Scheme 3). This new compound was characterized by spectroscopic means.

Several features of **10** are interesting (Fig. 3). First, there are four distinct methyl signals being observed in ^1H NMR, which implies that two chelated ligands, pyridinethiolates, are not



Scheme 3.

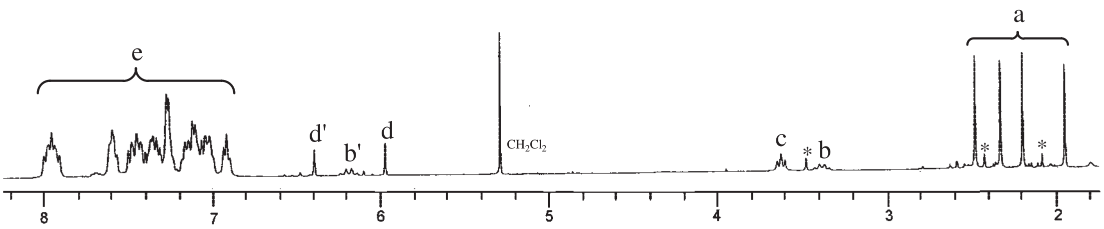


Fig. 3. ^{1}H NMR spectrum of **10** in $CDCl_3$ (300 MHz). a) –Me; b&b′: Ru–$PPh_2CH_2PPh_2$; c: Co_2–$PPh_2CH_2PPh_2$; d&d′: py; e: –Ph. Corresponding protons are in italics.

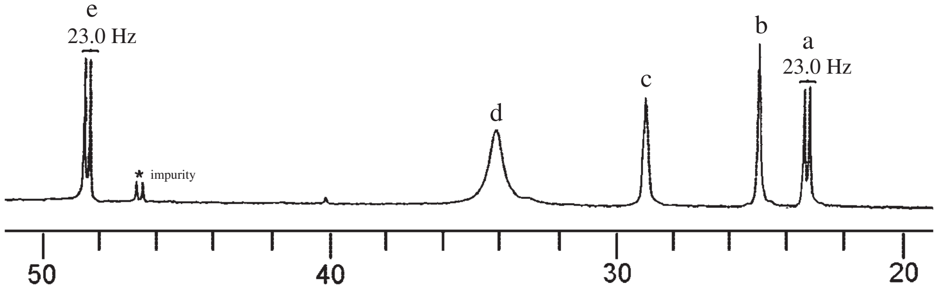


Fig. 4. ^{31}P NMR spectrum of **10** in $CDCl_3$ (121.44 MHz). a: P–Ru–*P* (from **8**); b: Ru–$PPh_2CH_2PPh_2$; c: N–Ru–*P* (from **8**); d: Co–$PPh_2CH_2PPh_2$; e: Ru–$PPh_2CH_2PPh_2$. Corresponding coordinated phosphines are in italics.

equivalent. Secondly, two sets of multiplets were observed at 6.20 ppm and 3.38 ppm for two matching methylene protons in **10**, which is an indication of a coordination of **8** to the ruthenium metal center.[1] In addition, the unusual downfield shift of one of the methylene protons, 6.20 ppm, implies that there is an intramolecular hydrogen bonding between the nitrogen atom of the pyridyl and the adjacent proton of the bridged dppm.[13] Thirdly, one set of triplets appears at 3.62 ppm, which is corresponding to the methylene protons of the bridged dppm. Finally, there are five signals, in the ratio of 1:2:1:1:1, observed for **10** in ^{31}P NMR (Fig. 4). Two sets of doublet peak were observed at 48.4 ppm and at 23.3 ppm, with the same coupling constants (23.0 Hz). It implies that two phosphorus atoms are in trans-positions. Interestingly, one dppm acts as a monodentate ligand toward the ruthenium metal center. The bridged dppm ligand must come from the fragmented **8**. Since the dppm takes one coordination position out of the metal center, one of the pyridinethiolates has to behave as a monodentate ligand, as shown.

Unfortunately, attempts to grow crystals from **10** failed. Tentative structural assignments of this new compound, based on spectroscopic data, are shown in Scheme 3. It is natural for us to assume that there an intermediate, **9**, is produced and then converted into **10** during long reaction hours. Compound **9** can be looked at as two carbonyls of **7** being replaced by a bidentate phosphine ligand, **8**.

Summary

The reaction of 3-cyano-4,6-dimethyl-pyridine-2-thiol with $Ru_3(CO)_{12}$ did not produce the expected sulfidotriruthenium carbonyl clusters. Rather, a pyridinethiolato-bridged, hydrido-bridged triruthenium carbonyl, $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **5**, as well as a bis(pyridinethiolato) chelated monoruthenium dicarbonyl complex, $[Ru(4,6\text{-CH}_3\text{-3-CN-py-}\kappa N\text{-thiol-}\kappa S)_2(CO)_2]$ **7**, were observed. Further reaction of **7** with a novel diphosphine ligand, $[Co_2(CO)_4\{\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2\}\{\mu\text{-PPh}_2\text{C}{\equiv}\text{CPPh}_2\}]$ **8**, resulted in the formation of a **8**-chelated mono-ruthenium carbonyl complex, $[Ru(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})(4,6\text{-CH}_3\text{-3-CN-2-S-py-}\kappa S)(PPh_2CH_2PPh_2)(\{\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2\}Co_2(CO)_4\{\mu\text{-PPh}_2\text{C}{\equiv}\text{CPPh}_2\})]$ **10**. Probably, an intramolecular hydrogen bonding is formed between the nitrogen atom of the pyridyl and the adjacent proton of the bridged dppm.

Experimental

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ^{1}H NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal TMS. ^{31}P and ^{13}C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. IR spectra of solution in CH_2Cl_2 were recorded on a Hitachi 270-30 spectrometer. Elemental analyses were recorded on a Heraeus CHN-O-S-Rapid. Accurate elemental analyses were precluded for some of the following compounds probably due to their chemical labilities.

Reaction of 3-Cyano-4,6-dimethyl-pyridine-2-thiol with $Ru_3(CO)_{12}$. Into a 100 cm^3 flask was placed $Ru_3(CO)_{12}$ (0.500 g, 0.782 mmol) with 3-cyano-4,6-dimethyl-2-mercaptopyridiene (0.128 g, 0.782 mmol) with 10 cm^3 of toluene. The solution was stirred at 55 °C for 20 h.

Subsequently, the resulting dark green solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography was carried out with a mixture solvent, CH_2Cl_2/hexanes = 1:1. The first yellow band was collected and identified as unreacted $Ru_3(CO)_{12}$. The second yellow band was eluted out and was characterized as $[Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **5** with 24% yield (0.141 g, 0.189 mmol). The third pale yellow band was tentatively assigned as $[Ru_3(CO)_9(\mu\text{-H})(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})]$ **6** with 23% yield (0.130 g, 0.181 mmol). The fourth pale yellow band was identified as $[Ru(4,6\text{-CH}_3\text{-3-CN-2-S-py})_2(CO)_2]$ **7** with 47% yield (0.180 g, 0.373 mmol).

Complex **5**: ^{1}H NMR ($CDCl_3$) δ 6.95 (s, 1H, arene), 2.51 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), −15.60 (hydride); ^{13}C NMR ($CDCl_3$) 204.13 (s, 1C, CO), 202.35 (s, 1C, CO), 198.96 (s, 1C, CO), 192.08 (s, 1C, CO), 185.97 (s, 1C, CO), 165.65 (s, 1C, ipso), 161.77 (s, 1C, arene), 152.34 (s, 1C, arene), 123.65 (s, 1C, arene), 115.44 (s, 1C, CN), 109.57 (s, 1C, arene), 23.06 (s, 1C, CH_3), 20.27 (s,1C, CH_3).

Complex **7**: ^{1}H NMR ($CDCl_3$) δ 6.51 (s, 2H, arene), 2.54 (s, 6H, CH_3), 2.40 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) 195.01 (s, 2C, CO), 184.73 (s, 2C, ipso), 163.56 (s, 2C, arene), 153.14 (s, 2C, arene), 119.37 (s, 2C, arene), 113.77 (s, 2C, CN), 108.90 (s, 2C, arene), 23.66 (s, 2C, CH_3), 20.43 (s, 2C, CH_3); Anal. Calcd: C, 44.71; H, 2.92; N, 11.59%; Found: C, 40.43; H, 2.76; N, 9.40%; IR (KBr) ν (cm^{-1}) 1996 (s, CO), 2057 (s, CO), 2221 (s, CN).

Reaction of $[Ru(4,6\text{-CH}_3\text{-3-CN-py-}\kappa\text{N-thiol-}\kappa\text{S})_2(CO)_2]$ 7 with $[Co_2(CO)_4\{\mu\text{-PPh}_2CH_2PPh_2\}\{\mu\text{-PPh}_2C\equiv CPPh_2\}]$ 8. The preparative procedure of **8** was described elsewhere.[1] Into a 100 cm^3 flask was placed **8** (0.700 g, 0.695 mmol) with **7** (0.336 g, 0.695 mmol) with 10 cm^3 of THF. The solution was stirred at 65 °C for 144 h. Similar procedures were taken as in the purification of **7**. The first purple band was eluted out and was characterized as the oxidized **8**. The second red band was eluted out and was characterized as $[Ru(\mu\text{-4,6-CH}_3\text{-3-CN-2-S-py})(4,6\text{-CH}_3\text{-3-CN-2-S-py-}\kappa\text{S})(PPh_2CH_2PPh_2)(\{\mu\text{-PPh}_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-PPh}_2\text{-}C\equiv CPPh_2\})]$ **10** with 24% yield (0.300 g, 0.169 mmol).

Complex **10**: ^{1}H NMR ($CDCl_3$) δ 8.00–6.90 (m, 60H, arene), 6.40 (s, 1H, pyridine), 5.97 (s, 1H, pyridine), 6.20 (m, 1H, CH_2), 3.62 (m, 2H, CH_2), 3.38 (m, 1H, CH_2), 2.48 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.95 (s, 3H, CH_3); ^{31}P NMR ($CDCl_3$) 48.4 (d, $J = 23.0$ Hz, 1P, dppm–Ru), 34.2 (s, 2P, dppm–Co), 29.0 (s, 1P, dppm), 25.0 (s, 1P, dppa), 23.3 (d, $J = 22.95$ Hz, 1P, dppa); Anal. Calcd: C, 63.33; H, 4.32; N, 3.08%; Found: C, 61.26; H, 4.19; N, 2.51%; IR (KBr) ν (cm^{-1}) 1982 (s, CO), 2009 (s, CO), 2038 (s, CN).

X-ray Crystallographic Studies. Suitable crystals of **5** and **7** were sealed in thin-walled glass capillaries under nitrogen atmosphere and were mounted on a Siemens Smart CCD diffractometer. The crystallographic data were collected using a θ–2θ scan mode with Mo Kα radiation. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package.[14] All the non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic parameters were used for H atoms that were refined using a riding model.[15] Crystallographic data of **5** and **7** are summarized in Table 1.

Supplementary Material. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no.198514 and 198515 for compounds **5** and **7**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

We thank the National Research Council of the R.O.C. (Grant NSC-91-2113-M-005-017) for support.

References

1 F.-E. Hong, Y.-C. Chang, R.-E. Chang, S.-C. Chen, and B.-T. Ko, *Organometallics*, **21**, 961 (2002).

2 M. D. Curtis, (Eds.), "Transition Metal Sulfur Chemistry: Biological and Industrial Significance," ed by E. I. Stiefel and K. Matsumoto, ACS, Washington, DC (1996), Chap. 8.

3 F.-E Hong, S.-C. Chen, Y.-T. Tsai, and Y.-C. Chang, *J. Organomet. Chem.*, **655**, 172 (2002).

4 a) A. J. Deeming, R. Ettore, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, **1971**, 1797. b) E. Sappa, O. Gambino, and G. Getini, *J. Organomet. Chem.*, **35**, 375 (1972).

5 R. D. Adams and D. A. Katahira, *Organometallics*, **1**, 53 (1982).

6 a) P. L. Andreu, J. A. Cabeza, V. Riera, Y. Jeannin, and D. Miguel, *J. Chem. Soc., Dalton Trans.*, **1990**, 2201. b) P. L. Andreu, J. A. Cabeza, J. M. Fernandez-Colinas, and V. Riera, *J. Chem. Soc., Dalton Trans.*, **1990**, 2927. c) S. Jeannin, Y. Jeannin, and G. Lavigne, *Inorg. Chem.*, **17**, 2103 (1978). d) A. J. Deeming, K. I. Hardcastle, and M. Karim, *Inorg. Chem.*, **31**, 4792 (1992). e) R. Dilshad, K. M. Hanif, M. B. Hursthouse, S. E. Kabir, K. M. A. Malik, and E. Rosenberg, *J. Organomet. Chem.*, **585**, 100 (1999). f) Y.-K. Au, K.-K. Cheung, and W.-T. Wong, *Inorg. Chim. Acta.*, **228**, 267 (1995). g) M. R. Churchill, J. W. Ziller, and J. B. Keister, *J. Organomet. Chem.*, **297**, 93 (1985).

7 J. A. Cabeza, *Eur. J. Inorg. Chem.*, **2002**, 1559.

8 a) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972). b) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).

9 Only limited spectroscopic data are available for **6**: ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 1H, arene), 2.88 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), −13.17 (hydride); Anal. Calcd: C, 28.38; H, 1.12; N, 3.89%; Found: C, 27.07; H, 1.47; N, 3.63%.

10 The averaged Co–Co and Ru–Ru bond lengths are 2.4 Å and 2.8 Å, respectively.

11 C. M. Lukehart, "Fundamental Transition Metal Organometallic Chemistry," Brools/Cole Publishing Company, Monterey, CA, (1985), Chap. 3.

12 a) S. G. Davies, "Organotransition Metal Chemistry Applications to Organic Synthesis," Pergamon Press (1982), Vol. 2. b) G. W. Parshall and S. D. Ittel, "Homogeneous Catalysis," 2nd ed, John Wiley & Sons, INC. (1992), Chap. 8. c) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977). d) "Applied Homogeneous Catalysis with Organometallic Compounds," ed by B. Cornils and W. A. Herrmann, VCH, New York (1996), Vols. 1 and 2. e) R. J. Puddephatt, *Coord. Chem. Rev.*, **33**, 149 (1980). f) R. Noyori, "Asymmetric Catalysis in Organic Synthesis," John Wiley & Sons, Inc. (1994). g) H. B. Kagan, "Asymmetric Synthesis Using Organometallic Catalysts," in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford (1982), Vol. 8, Chap. 53. h) "Comprehensive Asymmetric Catalysis," ed by E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Springer-Verlag, New York (1999), Vol. I.

13 a) C. E. Housecroft and E. C. Constable, "Chemistry: An Integrated Approach," Addison Wesley Longman Ltd. (1997), pp. 526. b) J. C. Kotz and P. Treichel, Jr., "Chemistry & Chemical Reactivity," Saunders College Publishing (1999), pp. 590.

14 G. M. Sheldrick, "SHELXTL PLUS User's Manual. Revision 4.1," Nicolet XRD Corporation, Madison, Wisconsin, USA (1991).

15 Hydrogen atoms were ride on carbons or oxygens in their idealized positions and held fixed with the C–H distances of 0.96 Å.