

Multifunctional Dithiocarbamates: Synthesis and Ring-Closing Metathesis of Diallyldithiocarbamate Complexes

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The complex cis-[RuCl₂(dppm)₂] reacts with the diallyldithiocarbamate $KS_2CN(CH_2CH=CH_2)_2$ to form $[Ru{S_2CN(CH_2CH=CH_2)_2}(dppm)_2]^+$. The same ligand was also used to prepare the alkenyl complexes $[RuR{S_2CN(CH_2CH=CH_2)_2}(CO)(PPh_3)_2](R = CH=CHBu^t, CH=CHC_6H_4Me-4,$ $C(C = CBu^{t}) = CHBu^{t}$ from the corresponding precursors $[RuRCl(CO)(BTD)(PPh_{3})_{2}]$ (BTD = 2,1,3benzothiadiazole) and $[Ru(C(C \equiv CBu^{t}) = CHBu^{t})Cl(CO)(PPh_{3})_{2}]$. The complexes $[Ni{S_{2}CN(CH_{2}-CHBu^{t})}]$ $CH=CH_2$ (dppp)]⁺ (dppp = 1,3-bis(diphenylphosphino)propane) and [M{S_2CN(CH_2CH=CH_2)_2}-(dppf)⁺ (M = Ni, Pd, Pt; dppf = 1,1'-bis(diphenylphosphino) ferrocene) were prepared from the respective precursors $[MCl_2(L_2)]$ (L₂ = dppp, dppf) and KS₂CN(CH₂CH=CH₂)₂ in the presence of NH_4PF_6 . In a similar manner, treatment of the cyclometalated dimer $[Pd(C, N-CH_2C_6H_4NMe_2)Cl]_2$ with the dithiocarbamate ligand yielded $[Pd(C, N-CH_2C_6H_4NMe_2){S_2CN(CH_2CH=CH_2)_2}]$. The homoleptic literature complexes $[Ni{S_2CN(CH_2CH=CH_2)_2}_2]$ and $[Co{S_2CN(CH_2CH=CH_2)_2}_3]$ were also prepared and characterized. Ring-closing metathesis catalyzed by [Ru(=CHPh)Cl₂(SIMes)(PCy₃)] converted [Ni{S₂CN(CH₂CH=CH₂)₂], [Pd(C,N-CH₂C₆H₄NMe₂){S₂CN(CH₂CH=CH₂)₂], [Ni{S₂CN-CH₂CH=CH₂)₂], $(CH_2CH=CH_2)_2(dppp)]^+, [Pt{S_2CN(CH_2CH=CH_2)_2}(dppf)]^+, [Ru{S_2CN(CH_2CH=CH_2)_2}^-)^-$ (dppm)₂]⁺, and [Ru(CH=CHC₆H₄Me-4){S₂CN(CH₂CH=CH₂)₂}(CO)(PPh₃)₂] into the corresponding 3-pyrroline dithiocarbamate compounds [Ni(S₂CNC₄H₆)₂], [Pd(C,N-CH₂C₆H₄NMe₂)(S₂CNC₄H₆)], $[Ni(S_2CNC_4H_6)(dppp)]^+$, $[Pt(S_2CNC_4H_6)(dppf)]^+$, $[Ru(S_2CNC_4H_6)(dppm)_2]^+$, and $[Ru(CH=CHC_6 H_4Me-4)(S_2CNC_4H_6)(CO)(PPh_3)_2]$, respectively. These complexes were also directly prepared from the reaction of the appropriate starting materials with preformed KS₂CNC₄H₆. The more sterically crowded complex $[Co{S_2CN(CH_2CH=CH_2)_2}]$ failed to give a reaction with the metathesis catalyst, although it could be prepared directly from $KS_2CNC_4H_6$ and cobalt acetate. The compounds $[Ru(CH=CHC_6 H_4Me-4$ {S₂CN(CH₂CH=CH₂)₂ (CO)(PPh₃)₂], [Ni{S₂CN(CH₂CH=CH₂)₂ (dppp)]PF₆, and [Ni(S₂- $CNC_4H_6)(dppp)$]PF₆ were characterized crystallographically.

Introduction

Since the advent of highly active catalysts with good functional group tolerance, alkene metathesis has rapidly become one of the most powerful tools in synthetic organic chemistry.¹ In particular, ring-closing metathesis (RCM) under mild conditions has provided easy access to small- or medium-sized rings and heterocycles, making it an invaluable tool in natural product synthesis.² However, the coordinatively unsaturated nature of the precatalysts used renders substrates which are capable of binding to the metal center problematic. For example, the metathesis of unsaturated molecules bearing unprotected amines can be undermined by coordination of the amine lone pair to the metal in competition with the alkene. A strategy often employed is the

use of electron-withdrawing substituents on the amine to tip the balance in favor of alkene coordination.^{3a,b} Another approach is to coordinate the amine lone pair to a Lewis acid such as $Ti(OPr^i)_4$ before metathesis is carried out.^{3c}

Our interest in secondary amines stems largely from their reaction with carbon disulfide to yield dithiocarbamate compounds, which have been widely used to coordinate transition metal ions. Indeed, dithiocarbamate complexes of transition metals have been known for over a century,⁴ but only rarely have the NR₂ substituents been exploited chemically.⁵ Coupling this potential to the well established attributes of dithiocarbamates (e.g., stabilization of a wide range of oxidation states⁶) provides a versatile class of ligand. In an attempt to exploit the potential of the substituents on nitrogen, we have

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investigated cyclic diamines, such as piperazine, to construct multimetallic compounds in a controlled, stepwise manner.^{7,8} This methodology has even been extended to the surface functionalization of nanoparticles.⁸ While functionalized dithiocarbamates can be used to incorporate different metals into the same system, they can also be used to modify the physical properties of the ligand, such as the protonation of amino groups to form water-soluble complexes.⁹

In the context of alkene metathesis, dithiocarbamates allow the delocalization of the lone pair of the parent amine, rendering the nitrogen nonbasic and thus enabling metathesis to occur. Herein we explore this potential in the context of our ongoing investigation of the reactivity of coordinated, functionalized dithiocarbamate ligands. Sporadic reports of complexes bearing the diallyldithiocarbamate ligand (Scheme 1) have appeared, mostly in the 1980s. These centered on homoleptic examples using simple metal salt precursors of iron,^{10a,b} cobalt,^{10a} nickel,^{10c} copper,^{10d} silver,¹¹ and gold.¹² Complexes bearing other coligands have received little attention. The work described here explores the synthesis and reactivity of such compounds and demonstrates that, once ligated to the metal center, the diallyl unit can enter into organic transformations such as alkene metathesis. This approach of using metathesis within the coordination sphere of a metal to create new ligand architectures has been elegantly demonstrated by Gladysz and co-workers over the past decade.¹³

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Scheme 1. The Dithiocarbamate Ligand Employed in This Work, Showing the Numbering Scheme Used for Spectroscopic Purposes



Results and Discussion

Synthesis of Diallyldithiocarbamate Complexes. The bis-(dppm) compound cis-[RuCl₂(dppm)₂]¹⁴ is a versatile starting material for the addition of bidentate chelates,^{7,15} and dithiocarbamates in particular.^{7,16} The facile removal of the chloride ligands allows the coordination of the new ligand, while the lack of lability of the dppm ligands inhibits further reactivity. The ligand KS₂CN(CH₂CH=CH₂)₂ was generated in situ by treatment of an aqueous solution of diallylamine with carbon disulfide in the presence of potassium hydroxide. Addition of an excess of this ligand to cis-[RuCl2- $(dppm)_2$ (dppm = bis(diphenylphosphino)methane) in the presence of NH₄PF₆ provided the pale yellow cation $[Ru{S_2CN(CH_2CH=CH_2)_2}(dppm)_2]PF_6$ (1) in 69% yield (Scheme 2). Two new pseudotriplets were observed in the ³¹P NMR spectrum at -18.4 and -5.3 ppm, showing coupling of 34.3 Hz. Further evidence for the retention of the dppm ligands was provided by the multiplet resonances for the methylene protons at 4.50 and 4.94 ppm in the ¹H NMR spectrum. The presence of the dithiocarbamate unit was confirmed by a multiplet at 4.09 ppm for the NCH₂ moiety, while the alkene protons were observed as resonances to lower field at 5.24 (= CH^{A}), 5.31 (= CH^{B}), and 5.61 (= CH^{C}) ppm. The overall composition was supported by a molecular ion in the electrospray mass spectrum (positive mode) at m/z1042 and good agreement of elemental analysis with calculated values.

Having established that the chelation chemistry of $[S_2CN-(CH_2CH=CH_2)_2]^-$ is shared with simple dithiocarbamates (e.g., coordination through sulfur), its reactivity was explored with group 8 alkenyl complexes.¹⁷ These compounds have experienced sustained interest based mainly on the complexes $[Ru(CR^1=CHR^2)Cl(CO)L_2]$ (L = PPrⁱ₃, ¹⁸ PPh₃¹⁹). Their popularity stems from the twin reactive sites of the alkenyl group and the metal center, making them ideal for the

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Scheme 2. Preparation of Diallyldithiocarbamate Complexes^a



 ${}^{a}R = Bu^{t}(2), C_{6}H_{4}Me-4(3); BTD = 2,1,3-benzothiadiazole.$

exploration of new ligands and bimetallic systems.¹⁸⁻²⁷ The most convenient triphenylphosphine-stabilized alkenyl complexes to use as starting materials are $[Ru(CR^1=CHR^2)Cl-(CO)(PPh_3)_2]^{19}$ and $[Ru(CR^1=CHR^2)Cl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole),^{24c} where BTD is a labile ligand. Although many ruthenium dithiocarbamates are known, no examples are known with the allyl-terminated ligands used here.

Addition of a slight excess of KS₂CN(CH₂CH=CH₂)₂ to an orange solution of [Ru(CH=CHBu^t)Cl(CO)(BTD)(PPh₃)₂] in dichloromethane led to rapid decolorization and formation of a yellow solution. Workup yielded a pale yellow product, which gave rise to a new singlet in the ³¹P NMR spectrum at 39.7 ppm. Evidence for the retention of the alkenyl ligand was provided by

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a singlet at 0.39 ppm in the ¹H NMR spectrum and resonances at 4.58 ($J_{\rm HP} = 1.8$ Hz) and 6.30 ppm ($J_{\rm HP} = 2.7$ Hz) showing mutual coupling of 16.4 Hz as well as coupling to the phosphorus nuclei. In addition, doublets at 3.31 and 3.79 ppm were observed for the inequivalent NCH₂ protons, while doublets for the allylic protons were noted at 4.74, 4.87, and 5.01 ppm as well as a multiplet for the =CH^C protons at 5.37 ppm. Infrared data displayed features typical of dithiocarbamate ($\nu_{\rm CN}$ at 1479 cm⁻¹) and triphenylphosphine ligands as well as an intense absorption at 1901 cm⁻¹ attributed to the carbonyl ligand. The overall formulation of [Ru(CH=CHBu^t){S₂CN-(CH₂CH=CH₂)₂}(CO)(PPh₃)₂] (**2**) was confirmed by an abundant molecular ion in the electrospray (positive ion) mass spectrum at *m/z* 909 and good agreement of elemental analysis with calculated values (Scheme 2).

In a similar fashion, the compounds $[Ru(CH=CHC_6H_4-Me-4){S_2CN(CH_2CH=CH_2)_2}(CO)(PPh_3)_2]$ (3) and $[Ru{C-(C=CBu^t)=CHBu^t}{S_2CN(CH_2CH=CH_2)_2}(CO)(PPh_3)_2]$ (4) were prepared in moderate yield. Spectroscopic and analytical data confirmed their formulations. Single crystals of 3 were grown and a structural study undertaken (Figure 1), the results of which are presented in the Structural Discussion.

In order to broaden the range of metals and coordination geometries investigated, a selection of group 10 compounds was chosen for reaction with the diallyldithiocarbamate ligand. The square-planar nickel complex [NiCl₂(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) was treated with an excess of KS₂CN(CH₂CH=CH₂)₂ in the presence of NH₄PF₆ to yield an orange complex, which was formulated as $[Ni{S_2CN(CH_2CH=CH_2)_2}(dppp)]PF_6$ (5). The diphosphine ligand gave rise to two multiplets in the ¹H NMR spectrum at 2.18 and 2.68 ppm alongside doublets at 4.15 ppm $(J_{\rm HH} = 6.2 \text{ Hz}), 5.23 (J_{\rm HH} = 17.1 \text{ Hz}), \text{ and } 5.33 \text{ ppm} (J_{\rm HH} =$ 10.2 Hz) and a multiplet at 5.67 ppm for the diallyldithiocarbamate ligand. The overall composition was supported by a molecular ion at m/z 642 and good agreement of elemental analysis with calculated values (Scheme 2). Single crystals of 5 were grown and a structural investigation undertaken (Figure 2 and Structural Discussion).

In a similar manner, the dppf (1,1'-bis(diphenylphosphino)-ferrocene) complexes of all three congeners of group 10, [M-{S₂CN(CH₂CH=CH₂)₂}(dppf)]PF₆ (M = Ni, **6**; M = Pd, **7**; M = Pt, **8**) were prepared from [MCl₂(dppf)]. These complexes shared similar spectroscopic features, with two broad singlets observed in each case for the cyclopentadienyl protons at 4.59

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Figure 1. Molecular structure of 3. Selected bond lengths (Å) and angles (deg): Ru-S(1) = 2.4999(5), Ru-S(3) = 2.4619(4), Ru-P(1) = 2.3689(5), Ru-P(2) = 2.3607(5), Ru-C(11) = 2.088(2), Ru-C(20) = 1.845(2), S(1)-C(2) = 1.713(2), C(2)-N(4) = 1.328(3), C(2)-S(3) = 1.707(2), C(6)-C(7) = 1.311(5), C(9)-C(10) = 1.308(4), C(11)-C(12) = 1.336(3); S(1)-Ru-S(3) = 70.296(16), P(1)-Ru-P(2) = 174.402(17), S(1)-C(2)-S(3) = 113.29(11), Ru-C(11)-C(12) = 125.77(15).



Figure 2. Molecular structure of the cation present in the crystals of 5. Selected bond lengths (Å) and angles (deg): Ni-S(1) = 2.2089(17), Ni-S(3) = 2.2097(17), Ni-P(11) = 2.1747(17), Ni-P(15) = 2.1788(17), S(1)-C(2) = 1.723(7), C(2)-N(4) = 1.314(8), C(2)-S(3) = 1.728(7), C(6)-C(7) = 1.304(11), C(9)-C(10) = 1.271(15); S(1)-Ni-S(3) = 79.24(6), P(11)-Ni-P(15) = 94.56(6), S(1)-C(2)-S(3) = 109.5(4).

and 4.69 ppm (6). The only unique feature was the J_{PtP} coupling of 3367 Hz observed in the ³¹P NMR spectrum for 8. An organometallic palladium example, [Pd(C,N-CH₂C₆H₄NMe₂)-{S₂CN(CH₂CH=CH₂)₂}] (9), was prepared from the [Pd(C,N-CH₂C₆H₄NMe₂)Cl]₂ dimer. In addition to resonances for the

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Figure 3. Steric profiles of coligand sets in the complexes chosen to investigate ring-closing metathesis ($R = C_6H_4$ Me-4).

 $[S_2CN(CH_2CH=CH_2)_2]^-$ chelate, the cyclometalated ligand gave rise to singlets at 2.93 and 4.02 ppm in the ¹H NMR spectrum for the methyl and methylene groups, respectively, and a multiplet for the aromatic protons.

Ring Closing of Diallyldithiocarbamate Complexes. As detailed in earlier work,^{7,8} our interest in introducing functionality into the pendant arms of dithiocarbamates is aimed at utilizing this additional center of reactivity within the complex. Having prepared a range of diallyl-substituted dithiocarbamate complexes, we sought to probe the chemistry of the pendant unsaturated units toward ring-closing metathesis.

In order to commence the investigation using relatively simple systems, the homoleptic compounds $[Ni{S_2CN(CH_2-CH=CH_2)_2}_2]$ (10) and $[Co{S_2CN(CH_2CH=CH_2)_2}_3]$ (11) were prepared by literature methods^{10a,c} and (hitherto unavailable) NMR data recorded.

In the complexes described here, the nitrogen lone pair is involved in bonding within the dithiocarbamate unit, leading to multiple-bond character in the N-C bond. This arrests free rotation around this linkage, meaning that the steric effects of the coligands could prove a significant factor in the ring-closing metathesis activity of the complexes described here. Figure 3 depicts the steric environment of the metal centers in this study (minus the diallydithiocarbamate ligand undergoing metathesis).

The square-planar complex 10 was treated with 5 mol % of the catalyst [Ru(=CHPh)Cl₂(SIMes)(PCy₃)] per dithiocarbamate ligand (hence 10 mol % overall) under nitrogen in dry, degassed dichloromethane. The reaction was monitored by ¹H NMR spectroscopy and, after 2 h, only trace amounts of the starting material were observed. Instead, a much simpler spectrum was revealed in which singlets at 4.36 and 5.91 ppm were observed for the methylene and alkene protons, respectively. The mass spectrum (ES positive mode) did not display a simple molecular ion but instead exhibited a peak for $2[M]^+$ at m/z 696. However, the formulation of the 3-pyrroline dithiocarbamate complex $[Ni(S_2CNC_4H_6)_2]$ (12), shown in Scheme 3, was supported by elemental analysis. Although the $[S_2CNC_4H_6]^-$ ligand has been prepared before, it has found most use in main-group compounds such as [O(SiMe₂CH₂)₂TeI(S₂CNC₄H₆)].²⁸ The ¹H NMR data for this compound consist of a broadened singlet at 4.50 ppm and a singlet at 5.92 ppm, values which are in good agreement with

those observed for **12**. As a further means to confirm the formulation, **12** was prepared through a different route, by direct reaction of Ni(OAc)₂ with an excess of preformed KS₂CNC₄-H₆.²⁸ Identical data were recorded for the compounds prepared by this alternative route.

The palladium compound $[Pd(C,N-CH_2C_6H_4NMe_2) \{S_2CN(CH_2CH=CH_2)_2\}$ (9) was also treated in the same way and resulted in complete conversion to the ring-closed product $[Pd(C,N-CH_2C_6H_4NMe_2)(S_2CNC_4H_6)]$ (13). A more complicated ¹H NMR spectrum was observed for 13, due to the unsymmetrical nature of the complex. A doublet and a multiplet at 4.56 ($J_{\rm HH} = 13.5 \, \text{Hz}$) and 5.97 ppm, respectively, were observed for the methylene and alkene protons, along with resonances for the cyclometalated ligand. A molecular ion was observed in the mass spectrum (ES positive mode) at m/z 385. The same product was also prepared using the direct method described above (Scheme 3). These successful reactions both involved sterically undemanding square-planar substrates; therefore, attention turned to the complex [Co{S₂- $CN(CH_2CH=CH_2)_{3}$ (11). After 2 h, no reaction was observed with 5 mol % catalyst loading per dithiocarbamate ligand. Higher loadings did not improve the situation. This remained the case after 24 h of stirring in dichloromethane at room temperature. The modest steric profile of the octahedral arrangement of three diallyldithiocarbamate ligands appeared sufficient to prevent coordination and subsequent metathesis of the alkene units by the ruthenium alkylidene catalyst. In order to test whether the product was unstable in some way, $[Co(S_2CNC_4H_6)_3]$ (14) was prepared directly from cobalt acetate and KS₂CNC₄H₆. ¹H NMR analysis of the product showed resonances for the 3-pyrroline dithiocarbamate ligand at 4.48 and 5.91 ppm, similar to the other complexes of this ligand prepared in this work. Mass spectrometry and elemental analysis data confirmed the formulation.

This result did not bode well for the other diallyldithiocarbamate complexes discussed earlier. After 2 h, no clear spectroscopic change (³¹P, ¹H NMR spectroscopy) was observed in the attempted ring-closing metathesis of [Ni{S₂CN(CH₂CH= CH₂)₂}(dppp)] (5) with 10 mol % of [Ru(=CHPh)Cl₂(SIMes)-(PCy₃)]; however, after the reaction was continued in dichloromethane at room temperature overnight, the resonances for the diallyldithiocarbamate ligand were replaced with singlets at 4.33 and 5.89 ppm. A very minor change in the chemical shift of the ³¹P NMR resonance to 12.5 ppm was discernible, despite the remoteness of the transformation from the phosphorus nuclei. Further spectroscopic and analytical data supported the formulation of the product as [Ni(S₂CNC₄H₆)(dppp)]PF₆ (**15**). Single crystals of this compound were grown and a structural

⁽²⁸⁾ Fuentes-Alemán, D.; Toscano, R.-A.; Muñoz-Hernández, M.; López-Cardoso, M.; García y García, P.; Cea-Olivares, R. J. Organomet. Chem. **2008**, 693, 3166–3170.





^{*a*}[Ru] catalyst = [Ru(=CHPh)Cl₂(SIMes)(PCy₃)]; BTD = 2,1,3-benzothiadiazole; L = PPh₃.

investigation undertaken (Figure 4 and Table 1). The salient features of this structure are discussed in the Structural Discussion.

Thus, it was proved that metathesis of the coordinated diallyldithiocarbamate ligand was possible despite the steric encumbrance introduced by the dppp ligand.

The same reactivity was found with $[Pt{S_2CN(CH_2CH=CH_2)_2}(dppf)]PF_6$ (8), which underwent ring-closing metathesis with 10 mol % $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$ overnight to give $[Pt(S_2CNC_4H_6)(dppf)]PF_6$ (16) in 89% yield. The ease with which this reaction proceeded illustrated that there appears to be no difference between the reactivity of firstand third-row transition-metal complexes. On steric grounds, the bis(dppm) complex $[Ru{S_2CN(CH_2CH=CH_2)_2}(dppm)_2]$ - PF_6 (1) appeared to be a much greater challenge, yet, after 24 h, conversion to $[Ru(S_2CNC_4H_6)(dppm)_2]PF_6$ (17) was shown to be complete (again with little evidence after 2 h) using 10 mol % of the catalyst. These results indicate that steric factors may slow the reaction but need not prevent RCM from taking place.

The previous examples all contain bidentate chelates (diphosphines or cyclometalated ligands), which confer substantial robustness on the substrates. Thus, the metathesis reaction was next investigated with $[Ru(CH=CHC_6H_4Me-4) \{S_2CN(CH_2CH=CH_2)_2\}(CO)(PPh_3)_2]$ (3), which only has monodentate ligands and bears an additional unsaturated organic functionality in the form of the alkenyl ligand. After 2 h, some evidence of transformation was present and, after a further 22 h, complete conversion had taken place to yield $[Ru(CH=CHC_6H_4Me-4)(S_2CNC_4H_6)(CO)(PPh_3)_2]$ (18). This species displayed a more complex ¹H NMR spectrum for the cyclized ligand due to the lack of symmetry in the molecule as a whole. Two broadened singlets were observed for the NCH₂ protons at 3.50 and 3.77 ppm, while the protons of the (Z)-alkene gave rise to a singlet resonance at 5.62 ppm. Infrared spectroscopy exhibited a v_{CO} absorption at 1912 cm⁻¹, and these data in favor of the given formulation were further corroborated by a molecular ion in the (ES positive mode) mass spectrum at m/z 915 and good agreement of elemental analysis with calculated values. To provide further chemical confirmation for compounds 12-18, they were all prepared directly from 3-pyrroline dithiocarbamate and an appropriate precursor. Spectroscopic data were found to be identical. It is worth noting that, for larger scale preparations, the RCM method is significantly cheaper due to the relative expense of 3-pyrroline.

Structural Discussion

A distorted-octahedral geometry is found for the ruthenium center in $[Ru(CH=CHC_6H_4Me-4){S_2CN(CH_2CH=CH_2)_2}(CO)(PPh_3)_2]$ (3) with cis-interligand angles in the



Figure 4. Molecular structure of one (A) of the two crystallographically independent cationic complexes present in the crystals of 15.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Two Crystallographically Independent Cationic Complexes (A and B) Present in the Crystals of 15

	А	В
$\overline{Ni(1)}-S(1)$	2.2158(7)	2.2286(7)
Ni(1) - P(9)	2.1740(7)	2.1697(7)
S(1) - C(2)	1.722(3)	1.716(3)
C(2) - S(3)	1.721(3)	1.717(3)
Ni(1) - S(3)	2.2300(7)	2.2277(7)
Ni(1) - P(13)	2.1654(7)	2.1775(7)
C(2) - N(4)	1.300(3)	1.309(3)
C(6) - C(7)	1.305(5)	1.311(5)
S(1) - Ni(1) - S(3)	79.45(3)	79.21(3)
S(1) - Ni(1) - P(13)	92.47(3)	93.26(3)
S(3) - Ni(1) - P(13)	169.03(3)	169.67(3)
S(1)-C(2)-S(3)	111.22(14)	111.65(15)
S(1) - Ni(1) - P(9)	172.64(3)	172.16(3)
S(3) - Ni(1) - P(9)	93.81(3)	93.01(3)
P(9) - Ni(1) - P(13)	93.81(3)	94.33(3)

range 70.296(16)–102.77(6)°. The Ru–S distances of 2.4619(4) and 2.4999(5) Å are marginally shorter than those of 2.466(1) and 2.508(1) Å found in $[Ru{C(\Xi CPh)= CHPh}{(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2}]Cl,^{7c}$ though in both compounds the greater trans influence of the alkenyl ligand over that of the carbonyl is reflected in the elongation of the Ru–S bond trans to it. The S(3)–C(2)–S(1) angle of 113.29(11)° is slightly smaller than that of 114.6(3)° observed for the literature complex, while the S(3)–Ru–S(1) angle of 70.296(16)° is the same as that of 70.33(4)° found in the enynyl compound. The C(2)–N(4) distance of 1.328(3) Å indicates significant double-bond character,²⁹ restricting rotation and causing near-planarity of the RuS₂CNR₂ unit. The bond data for the alkenyl ligand itself are unremarkable and compare well with previous examples in the literature.²⁴ⁱ

The geometry at the nickel center in the structure of [Ni- $\{S_2CN(CH_2CH=CH_2)_2\}(dppp)]PF_6$ (5) is distorted square

planar, and thus the steric bulk of the phosphine ligand is distal to the dithiocarbamate moiety (in contrast to the structure of **3**). The coordination plane is markedly distorted, with S(1) lying ca. 0.51 Å out of the {Ni,S(3),P(11), P(15)} plane, the atoms of which are coplanar to within ca. 0.03 Å. Other data are similar to previous examples of nickel dithiocarbamate compounds in the literature, such as $[Ni(S_2CNC_4H_8NH_2)(dppp)]^{2+}$.^{7b}

 $[Ni(S_2CNC_4H_6)(dppp)]PF_6$ (15) crystallized with two independent cation: anion pairs (A and B) in the asymmetric unit. Complex cation A is shown in Figure 4, while B is shown in Figure S4 in the Supporting Information. The geometry at the nickel center is distorted square planar, with P(13) lying ca. 0.22 Å [0.25 Å] out of the {Ni,S(1),S(3),P(9)} plane, the atoms of which are coplanar to within ca. 0.04 Å [0.01 Å] (the values in brackets refer to cation B). One interesting oddity of the two independent cations is that in 15-B the two Ni-S bonds are the same [2.2286(7) and 2.2277(7) Å], but in 15-A they are statistically significantly different [2.2158(7) and 2.2300(7) A]; it is the bond to S(1)that is anomalously short. There is no obvious reason the bonding should be different between the two independent complexes. The bite angle of the dithiocarbamate ligand, S(1)-Ni(1)-S(3), is 79.45(3) and 79.21(3)° for the two independent molecules in the structure, which are close to that of 79.68(7)° for $[Ni(S_2CNC_4H_8NH_2)(dppp)]^{2+.7b}$ The C(6)-C(7) distances of 1.305(5) and 1.311(5) Å are consistent with the presence of a double bond.

The C–S bonds across all three structures are in the range 1.707(2)-1.728(7) Å, while the C(2)–N(4) bonds show a greater deviation, ranging between 1.300(3) and 1.328(3) Å.

Conclusion

The diallyldithiocarbamate complexes described here ably demonstrate the potential of dithiocarbamates to introduce a further reactive site into metal complexes. Previously, only simple, homoleptic compounds of this dithiocarbamate ligand have been reported, but this work demonstrates its coordination to octahedral ruthenium σ -alkenyl and bis-(dppm) compounds as well as examples of all three group 10 metals. The potential of the pendant allyl units to allow further modification of the compounds has been shown in the ring-closing metathesis of six examples of Ru, Ni, Pd, and Pt to generate cyclic dithiocarbamate ligands in situ. These reactions proceeded cleanly (and in some cases rapidly) under mild conditions, showing surprisingly limited dependence on the steric environment. The failure of the cobalt-(III) complex 10 to undergo reaction will be examined further, both by experiment and computation, to probe the contribution of steric and electronic effects. Having demonstrated the viability of this approach, work is underway to investigate the cross-metathesis of metal dithiocarbamate units.

Experimental Section

General Comments. Experiments to form 1-11 and all reactions using KS₂CNC₄H₆ were carried out under aerobic conditions, while the metathesis reactions were conducted under nitrogen using degassed dichloromethane. All the complexes appear indefinitely stable toward the atmosphere in solution and in the solid state. The compounds [Ru(CH=CHBu^t)-Cl(CO)(BTD)(PPh₃)₂], [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)-(PPh₃)₂], and [Ru(CH=CHCPh₂OH)Cl(BTD)(CO)(PPh₃)₂]

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were prepared in a manner identical with that for the corresponding BSD (2,1,3-benzoselanadiazole) complexes.^{24c} The following complexes have been described elsewhere: $[Ru\{C(C \equiv CBu^{t})=CHBu^{t}\}Cl(CO)(PPh_{3})_{2}]^{,30}$ *cis*- $[RuCl_{2}(dppm)_{2}]^{,14b}$ $[MCl_{2}-(dppf)]$ $(M = Ni,^{31} Pd,^{32} Pt^{33})$, $[NiCl_{2}(dppp)]^{,34}$ $[Pd(C,N-CH_{2}C_{6}-H_{4}NMe_{2})Cl]_{2}^{,35}$ and $[Ru(=CHPh)Cl_{2}(SIMes)(PCy_{3})]^{,36}$ Solutions (4.0 mmol) of the ligand KS₂CN(CH₂CH=CH₂)¹⁰ were prepared in water. Other reagents and solvents were used as received from commercial sources. Petroleum ether refers to the fraction boiling at 40-60 °C. Electrospray mass spectrometry data were obtained using a Micromass LCT Premier instrument, and infrared data were measured using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Characteristic phosphine-associated infrared data were observed in all relevant complexes but have been omitted for reasons of brevity. NMR spectroscopy was performed at 25 °C using a Bruker AV400 spectrometer. All couplings are in hertz, and ³¹P NMR spectra are proton-decoupled. Resonances for the hexafluorophosphate anion are not reported. Elemental analysis data were obtained from London Metropolitan University. For the ring-closed products, further purification to remove remaining ruthenium catalyst was achieved by careful recrystallization from dichloromethane and diethyl ether to provide materials of sufficient purity for synthetic and spectroscopic purposes.

General Procedure for Reactions of Metal Complexes with $KS_2CN(CH_2CH=CH_2)_2$. A fresh solution of $KS_2CN(CH_2CH=$ CH₂)₂ in water (30 mL) was prepared by stirring diallylamine (1.00 mL, 6.371 mmol) and CS₂ (0.42 mL, 6.984 mmol) in the presence of KOH (393 mg, 7.004 mmol) for 40 min.⁹ Assuming complete conversion, appropriate portions of this solution were added by syringe to a solution of the metal complex in acetone and dichloromethane (20 mL/10 mL). The reaction mixture was stirred for 20 min. All solvent was removed, the crude product was dissolved in dichloromethane (15 mL), and this solution was filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed, diethyl ether (20 mL) was added, and the crude product was triturated ultrasonically. The pale yellow precipitate was filtered and washed with water (5 mL) and diethyl ether (10 mL). The product was dried under vacuum. Note: the preparation of the ligand as a methanolic solution led to substantial contamination of the alkenyl complexes with the corresponding methyl xanthate species [Ru(alkenyl)- $(S_2COMe)(CO)(PPh_3)_2$, through attack of deprotonated solvent on CS₂ and subsequent coordination.

 $[Ru{S_2CN(CH_2CH=CH_2)_2}(dppm)_2]PF_6$ (1). A solution of *cis*- $[RuCl_2(dppm)_2]$ (200 mg, 0.213 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 2 equiv of the dithiocarbamate ligand and NH₄PF₆ (69 mg, 0.423 mmol) in water (5 mL), and the reaction mixture was stirred for 30 min. All solvent was removed, the residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed, diethyl ether (30 mL) was added, and the solid was triturated ultrasonically. The pale yellow product was washed with water (10 mL) and

diethyl ether (10 mL) and dried under vacuum. Yield: 175 mg (69%). IR (solid state): 1482, 1435, 1414, 1244, 1098, 999, 928, 833 ($\nu_{\rm PF}$), 739, 727, 694 cm⁻¹. ³¹P NMR (CD₂Cl₂): -18.4, -5.3 (t × 2, dppm, $J_{\rm HH}$ = 34.3 Hz). ¹H NMR (CD₂Cl₂): 4.09 (m, 4H, NCH₂); 4.50, 4.94 (m × 2, 2 × 2H, PCH₂P); 5.24 (d, 2H, =CH^A, $J_{\rm HH}$ = 17.0 Hz); 5.31 (d, 2H, =CH^B, $J_{\rm HH}$ = 10.1 Hz); 5.61 (m, 2H, =CH^C); 6.49, 6.99, 7.11, 7.27–7.51, 7.71 (m × 5, 40H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 1042 (100) [M]⁺. Anal. Calcd for C₅₇H₅₄F₆NP₅RuS₂ (M_w = 1187.11): C, 57.7; H, 4.6; N, 1.2. Found: C, 57.7; H, 4.5; N, 1.1.

[**Ru**(CH=CHBu¹){S₂CN(CH₂CH=CH₂)₂}(CO)(PPh₃)₂] (2). [Ru(CH=CHBu¹)Cl(CO)(BTD)(PPh₃)₂] (100 mg, 0.110 mmol) gave 63 mg of pale yellow product (63%). IR (solid state): 1901 (ν_{CO}), 1642, 1479, 1410, 1358, 1227, 982, 916 cm⁻¹. ³¹P NMR (CDCl₃): 39.7 (s, PPh₃). ¹H NMR (CDCl₃): 0.39 (s, 9H, CCH₃); 3.31 (d, 2H, NCH₂, $J_{HH} = 6.2$ Hz); 3.79 (d, 2H, NCH₂, $J_{HH} = 6.0$ Hz); 4.58 (dt, 1H, H β , $J_{HH} = 16.4$ Hz, $J_{HP} = 1.8$ Hz); 4.74 (d, 1H, =CH^A, $J_{HH} = 17.0$ Hz); 4.87 (d, 1H, =CH^A, $J_{HH} = 17.1$ Hz); 5.01 (d, 2H, =CH^B, $J_{HH} = 10.2$ Hz); 5.37 (m, 2H, =CH^C); 6.29 (dt, 1H, H α , $J_{HH} = 16.4$ Hz, $J_{HP} = 2.7$ Hz); 7.29–7.36, 7.56–7.61 (m × 2, 30H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 909 (71) [M]⁺; 826 (58) [M – alkenyl]⁺. Anal. Calcd for C₅₀H₅₁NOP₂RuS₂ ($M_w = 909.10$): C, 66.1; H, 5.7; N, 1.5. Found: C, 65.9; H, 5.6; N, 1.6.

[**Ru**(CH=CHC₆H₄Me-4){S₂CN(CH₂CH=CH₂)₂}(CO)(PPh₃)₂] (3). [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] (100 mg, 0.106 mmol) gave 61 mg of pale yellow product (61%). IR (solid state): 1094 (ν_{CO}), 1710, 1643, 1548, 1410, 1277, 1230, 1127, 981, 968, 935, 920, 827 cm⁻¹. ³¹P NMR (CDCl₃): 39.3 (s, PPh₃). ¹H NMR (CDCl₃): 2.24 (s, 3H, CCH₃); 3.53 (d, 2H, NCH₂, J_{HH} = 5.3 Hz); 3.80 (d, 2H, NCH₂, J_{HH} = 6.0 Hz); 4.81 (d, 1H, =CH^A, J_{HH} = 17.1 Hz); 4.86 (d, 1H, =CH^A, J_{HH} = 17.4 Hz); 5.00 (d, 2H, =CH^B, J_{HH} = 10.2 Hz); 5.25 (m, 2H, =CH^C); 5.53 (d, 1H, H^β, J_{HH} = 16.7 Hz); 6.38, 6.83 (AB, 4H, C₆H₄, J_{AB} = 8.0 Hz); 7.28–7.36, 7.55–7.59 (m × 2, 30H, C₆H₅); 7.71 (dt, 1H, Hα, J_{HH} = 16.7 Hz, J_{HP} = 3.2 Hz) ppm. MS (ES positive): *m*/*z* (abundance) 943 (5) [M]⁺; 826 (32) [M – alkenyl]⁺. Anal. Calcd for C₅₃H₄₉NOP₂RuS₂ (M_w = 943.11): C, 67.5; H, 5.2; N, 1.5. Found: C, 67.4; H, 5.2; N, 1.6.

[**Ru**(**C**(**C**≡**CBu**^t)=**CHBu**^t){**S**₂**CN**(**CH**₂**CH**=**CH**₂)₂}(**CO**)-(**PPh**₃)₂] (4). [Ru(**C**(**C**≡**CBu**^t)=**CHBu**^t)**C**(**CO**)(**PPh**₃)₂] (100 mg, 0.117 mmol) gave 32 mg of pale yellow product (28%). IR (solid state): 2162 (ν_{C} =**C**), 1921 (ν_{CO}), 1640, 1464, 1410, 1356, 1228, 1186, 992, 920, 828 cm⁻¹. ³¹P NMR (CDCl₃): 38.3 (s, PPh₃). ¹H NMR (CDCl₃): 0.61 (s, 9H, Bu^t); 1.59 (s, 9H, Bu^t); 3.48 (m, 2H, NCH₂); 3.59 (d, 2H, NCH₂, J_{HH} = 6.2 Hz); 4.81 (d, 1H, =**CH**^A, J_{HH} = 17.0 Hz); 4.86 (d, 1H, =**CH**^A, J_{HH} = 17.0 Hz); 4.98 (d, 2H, =**CH**^B, J_{HH} = 10.1 Hz); 5.17 (m, 2H, =**CH**^C); 5.22 (s, 1H, H^β); 7.26−7.36, 7.60 (m × 2, 30H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 990 (32) [M]⁺; 826 (20) [M − alkenyl]⁺. Anal. Calcd for C₅₆H₅₉-NOP₂RuS₂·3.25CH₂Cl₂ (M_w = 989.22): C, 56.2; H, 5.2; N, 1.1. Found: C, 56.0; H, 4.8; N, 1.5.

 $[Ni{S_2CN(CH_2CH=CH_2)_2}(dppp)]PF_6$ (5). A solution of [NiCl₂(dppp)] (200 mg, 0.369 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equiv of KS2CN- $(CH_2CH=CH_2)_2$ and NH_4PF_6 (120 mg, 0.736 mmol) in water (5 mL), and the reaction mixture was stirred for 30 min. All solvent was removed, the residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl, excess NH₄PF₆, and ligand. All solvent was again removed, petroleum ether (30 mL) was added, and the solid was triturated ultrasonically. The orange product was washed with water (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 212 mg (73%). IR (solid state): 1515, 1435, 1418, 1242, 1177, 1100, $\overline{971}$, 938, 824 ($\nu_{\rm PF}$), 742, 691 cm⁻¹. ³¹P NMR (CDCl₃): 12.8 (s, dppp). ¹H NMR (CDCl₃): 2.18 (m, 2H, dppp-CH₂); 2.68 (m, 4H, dppp-PCH₂); 4.15 (d, 4H, NCH₂, $J_{HH} = 6.2$ Hz); 5.23 (d, 2H, =CH^A, $J_{HH} = 17.1$ Hz); 5.33 (d, 2H, =CH^B, $J_{HH} = 10.2$ Hz); 5.67 (m, 2H, =CH^C); 7.40 – 7.62 (m, 20H, C₆H₅) ppm. MS (ES +positive): m/z (abundance) 642 (100) [M]⁺. Anal. Calcd

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for $C_{34}H_{36}F_6NNiP_3S_2$ ($M_w = 788.39$): C, 51.8; H, 4.6; N, 1.8. Found: C, 52.0; H, 4.7; N, 1.8.

[Ni{S₂CN(CH₂CH=CH₂)₂}(dppf)]PF₆ (6). A solution of [NiCl₂(dppf)] (100 mg, 0.146 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equiv of KS₂CN-(CH₂CH=CH₂)₂ and NH₄PF₆ (48 mg, 0.295 mmol) in water (5 mL), and the reaction mixture was stirred for 30 min. All solvent was removed, the residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl, excess NH₄PF₆, and ligand. All solvent was again removed, petroleum ether (30 mL) was added, and the solid was triturated ultrasonically. The orange product was washed with water (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 130 mg (96%). IR (solid state): 1528, 1500, 1481, 1434, 1240, 1164, 1094, 1025, 976, 932, 830 ($\nu_{\rm PF}$), 742, 697 cm⁻¹. ³¹P NMR $(d_6$ -acetone): 31.1 (s, dppp). ¹H NMR (d_6 -acetone): 4.25 (d, 4H, NCH₂, $J_{HH} = 6.0$ Hz); 4.59, 4.69 (s(br) × 2, 2 × 4H, C₅H₄); 5.23 (d, 2H, =CH^A, $J_{HH} = 17.2$ Hz); 5.29 (d, 2H, =CH^B, $J_{HH} = 10.0$ Hz); 5.73 (m, 2H, =CH^C); 7.35–7.96 (m, 20H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 785 (100) [M]⁺. Anal. Calcd for $C_{41}H_{38}F_6FeNNiP_3S_2$ ($M_w = 930.33$): C, 52.9; H, 4.1; N, 1.5. Found: C, 52.8; H, 4.0; N, 1.5.

 $[Pd{S_2CN(CH_2CH=CH_2)_2}(dppf)]PF_6$ (7). A solution of [PdCl₂(dppf)] (50 mg, 0.068 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equiv of KS₂CN- $(CH_2CH=CH_2)_2$ and NH_4PF_6 (22.4 mg, 0.137 mmol) in water (5 mL), and the reaction mixture was stirred for 30 min. All solvent was removed, the residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl, excess NH₄PF₆, and ligand. All solvent was again removed, petroleum ether (30 mL) was added, and the solid was triturated ultrasonically. The orange product was washed with water (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 60 mg (90%). IR (solid state): 1522, 1482, 1436, 1309, 1243, 1168, 1096, 997, 984, 830 ($\nu_{\rm PF}$), 757, 742, 698 cm⁻¹. ³¹P NMR (d_6 acetone): 32.3 (dppf). ¹H NMR (d_6 -acetone): 4.33 (d, 4H, NCH₂,, $J_{HH} = 6.0$ Hz); 4.59, 4.74 (s(br) × 2, 2 × 4H, C₅H₄); 5.27 (d, 2H, =CH^A, $J_{HH} = 17.2$ Hz); 5.31 (d, 2H, =CH^B, $J_{HH} = 10.5$ Hz); 5.77 (m, 2H, =CH^C); 7.59–7.82 (m, 20H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 832 (100) [M]⁺. Anal. Calcd for $C_{41}H_{38}F_6FeNP_3S_2$ ($M_w = 978.06$): C, 50.3; H, 3.9; N, 1.4. Found: C, 50.4; H, 4.0; N, 1.5.

 $[Pt{S_2CN(CH_2CH=CH_2)_2}(dppf)]PF_6$ (8). A solution of [PtCl₂(dppf)] (100 mg, 0.122 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 1.5 equiv of KS₂CN-(CH₂CH=CH₂)₂ and NH₄PF₆ (40 mg, 0.245 mmol) in water (5 mL), and the reaction mixture was stirred for 30 min. All solvent was removed, the residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl, excess NH₄PF₆, and ligand. All solvent was again removed, petroleum ether (30 mL) was added, and the solid was triturated ultrasonically. The orange product was washed with water (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 125 mg (96%). IR (solid state): 1528, 1483, 1436, 1411, 1245, 1194, 1168, 1098, 1026, 997, 942, 829 ($\nu_{\rm PF}$), 757, 699, 690 cm⁻¹. ³¹P NMR (CDCl₃): 15.9 (dppf, J_{PtP} = 3367 Hz). ¹H NMR (CDCl₃): 4.11 (d, 4H, NCH₂, J_{HH} = 6.2 Hz); 4.41, 4.60 (s(br) × 2, 2 × 4H, C₅H₄); 5.24 (d, 2H, =CH^A, J_{HH} = 17.1 Hz); 5.34 (d, 2H, =CH^B, J_{HH} = 10.0 Hz); 5.67 (m, 2H, =CH^C); 7.49–7.69 (m, 20H, C_6H_5) ppm. MS (ES positive): m/z (abundance) 921 (100) [M]⁺. Anal. Calcd for $C_{41}H_{38}F_6FeNP_3PtS_2$ ($M_w = 1066.71$): C, 46.2; H, 3.6; N, 1.3. Found: C, 46.0; H, 3.6; N, 1.3.

 $[Pd(C,N-CH_2C_6H_4NMe_2){S_2CN(CH_2CH=CH_2)_2}]$ (9). A solution of $[Pd(C,N-CH_2C_6H_4NMe_2)Cl]_2$ (200 mg, 0.362 mmol) in acetone (20 mL) and dichloromethane (10 mL) was treated with 3 equiv of KS_2CN(CH_2CH=CH_2)_2, and the reaction mixture was stirred for 30 min. All solvent was removed, the

residue was dissolved in the minimum volume of dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed, petroleum ether (30 mL) was added, and the solid was triturated ultrasonically. The orange product was washed with water (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 258 mg (86%). IR (solid state): 1488, 1407, 1343, 1329, 1280, 1249, 1177, 1139, 1112, 1044, 1022, 992, 973, 926, 870, 852, 750 cm⁻¹. ¹H NMR (CDCl₃): 2.93 (s, 6H, NMe₂); 4.02 (s, 2H, CH₂Pd); 4.43 (m, 4H, NCH₂); 5.26 (d, 2H, =CH^B, J_{HH} = 10.2 Hz); 5.29–5.34 (m, 2H, =CH^A); 5.84 (m, 2H, =CH^C); 6.94–7.05 (m, 4H, C₆H₄) ppm. MS (ES positive): m/z (abundance) 413 (100) [M]⁺. Anal. Calcd for C₁₆H₂₂N₂PdS₂ (M_w = 412.91): C, 46.5; H, 5.4; N, 6.8. Found: C, 46.5; H, 5.3; N, 6.8.

[Ni{S₂CN(CH₂CH=CH₂)₂] (10). This compound was prepared using the literature procedure. ⁸ ¹H NMR (CDCl₃): 4.19 (d, 8H, NCH₂, $J_{HH} = 5.6$ Hz); 5.25 (d, 4H, =CH^A, $J_{HH} = 17.1$ Hz); 5.31 (d, 4H, =CH^B, $J_{HH} = 10.1$ Hz); 5.76 (m, 4H, =CH^C) ppm.

[Co{S₂CN(CH₂CH=CH₂)₂]₃] (11). This compound was prepared using the literature procedure.⁹ ¹H NMR (CDCl₃): 4.19, 4.44 (dd $\times 2, 2 \times 6$ H, NCH₂, $J_{HH} = 15.0, 5.1$ Hz); 5.25–5.29 (m, 12H, =CH^{A/B}); 5.82 (m, 6H, =CH^C) ppm.

Preparation of KS₂CNC₄H₆. An aqueous solution (30 mL) of 3-pyrroline (40 mg, 0.579 mmol) and KOH (32.5 mg, 0.579 mmol) was stirred for 10 min and then treated with carbon disulfide (52.8 mg, 0.693 mmol). After it was stirred for a further 40 min, the solution was used for the additions to the metal complexes.

 $[Ni(S_2CNC_4H_6)_2]$ (12). (a) Compound 10 (40 mg, 0.099 mmol) and $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$ (8.4 mg, 0.010 mmol) were dissolved in dry, degassed dichloromethane (20 mL) and stirred for 2 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a greenbrown product, which was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 28 mg (81%).

(b) [Ni(OAc)₂] (20 mg, 0.113 mmol) was dissolved in dichloromethane (10 mL) and acetone (20 mL) and treated with an aqueous solution of KS₂CNC₄H₆ (0.170 mmol). The reaction mixture was stirred for 1 h and all solvent removed. The crude product was dissolved in dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed and ultrasonic trituration in diethyl ether (20 mL) used to obtain a green-brown product. Yield: 30 mg (77%). IR (solid state): 1625, 1497, 1434, 1351, 1326, 1187, 995, 930, 895, 755 cm⁻¹. ¹H NMR (CDCl₃): 4.36 (s, 8H, NCH₂); 5.91 (s, 4H, HC=CH) ppm. MS (ES positive): m/z (abundance) 696 (100) 2[M]⁺. Anal. Calcd for C₁₀H₁₂N₂NiS₄ ($M_w = 347.17$): C, 34.6; H, 3.5; N, 8.1. Found: C, 34.8; H, 3.5; N, 8.0.

 $[Pd(C,N-CH_2C_6H_4NMe_2)(S_2CNC_4H_6)]$ (13). (a) Compound 9 (40 mg, 0.097 mmol) and $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$ (4.1 mg, 0.005 mmol) were dissolved in dry, degassed dichloromethane (20 mL), and this solution was stirred for 2 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a pale brown product, which was washed with petroleum ether (20 mL) and dried under vacuum. Yield: 26 mg (70%).

(b) The same procedure as for **12** was employed using $[Pd(C,N-CH_2C_6H_4NMe_2)Cl]_2$ (20 mg, 0.036 mmol) and KS₂CNC₄H₆ (0.109 mmol) with trituration in petroleum ether (20 mL) to yield a pale brown product. Yield: 19 mg (69%). IR (solid state): 1577, 1501, 1449, 1354, 1188, 1105, 1045, 1027, 989, 929, 869, 849, 737 cm⁻¹. ¹H NMR (CDCl₃): 2.94 (s, 6H, NMe₂); 4.03 (s, 2H, CH₂Pd); 4.56 (d, 4H, NCH₂, $J_{HH} = 13.5$ Hz); 5.97 (m, 2H, HC=CH); 6.94–7.04 (m, 4H, C₆H₄) ppm. MS (ES positive): m/z (abundance) 385 (100) [M]⁺. Anal. Calcd for C₁₄H₁₈N₂PdS₂ ($M_w = 384.86$): C, 43.7; H, 4.7; N, 7.3. Found: C, 43.8; H, 4.7; N, 7.2.

 $[Co(S_2CNC_4H_6)_3]$ (14). $[Co(O_2CMe)_2] \cdot 4H_2O$ (100 mg, 0.401 mmol) was dissolved in water (20 mL) and treated with an aqueous solution of KS₂CNC₄H₆ (1.606 mmol). The reaction mixture was stirred for 3 h and all solvent removed. The crude product was dissolved in dichloromethane, and this solution was filtered through diatomaceous earth (Celite). All solvent was again removed and

ultrasonic trituration in diethyl ether (20 mL) used to obtain a green product. Yield: 192 mg (97%). IR (solid state): 1572, 1475, 1428, 1351, 1193, 1171, 1102, 1008, 990, 930, 761 cm⁻¹. ¹H NMR (CDCl₃): 4.48 (s(br), 12H, NCH₂); 5.91 (s(br), 6H, HC=CH) ppm. MS (ES positive): m/z (abundance) 1005 (65) [2 M + Na]⁺, 514 (4) [M + Na]⁺. Anal. Calcd for C₁₅H₁₈CoN₃S₆ (M_w = 491.65): C, 36.6; H, 3.7; N, 8.6. Found: C, 36.6; H, 3.7; N, 8.5.

 $[Ni(S_2CNC_4H_6)(dppp)]PF_6$ (15). (a) Compound 5 (40 mg, 0.051 mmol) and $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$ (4.3 mg, 0.005 mmol) were dissolved in dry, degassed dichloromethane (20 mL), and this solution was stirred for 24 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a green-brown product, which was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 26 mg (67%).

(b) [NiCl₂(dppp)] (20 mg, 0.037 mmol) was dissolved in dichloromethane (10 mL) and acetone (20 mL) and treated with an aqueous solution of $KS_2CNC_4H_6$ (0.056 mmol) followed by NH₄PF₆ (12 mg, 0.074 mmol) in water (0.5 mL). The reaction mixture was stirred for 1 h and all solvent removed. The crude product was dissolved in dichloromethane, and this solution was filtered through diatomaceous earth (Celite) to remove KCl and excess ligand. All solvent was again removed and ultrasonic trituration in diethyl ether (20 mL) used to obtain a green-brown product. Yield: 26 mg (92%). IR (solid state): 1631, 1522, 1485, ¹452, 1435, 1355, 1264, 1184, 1160, 1100, 998, 972, 931, 831 (ν_{PF}) cm⁻¹. ³¹P NMR (CDCl₃): 12.5 (s, dppp). ¹H NMR (CDCl₃): 2.19 (m, 2H, dppp-CCH₂C); 2.70 (m, 4H, dppp-PCH₂); 4.33 (s(br), 4H, NCH₂); 5.89 (s, 2H, HC=CH); 7.43-7.63 (m, 20H, C_6H_5) ppm. MS (ES positive): m/z (abundance) 614 (100) [M]⁺. Anal. Calcd for $C_{32}H_{32}F_6NNiP_3S_2$ ($M_w = 760.34$): C, 50.6; H, 4.2; N, 1.8. Found: C, 50.7; H, 4.3; N, 1.9.

[Pt($S_2CNC_4H_6$)(dppf)]PF₆ (16). (a) Compound 8 (40 mg, 0.038 mmol) and [Ru(=CHPh)Cl₂(SIMes)(PCy₃)] (3.2 mg, 0.004 mmol) were dissolved in dry, degassed dichloromethane (20 mL), and the mixture was stirred for 24 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a yellow product, which was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 35 mg (89%).

(b) The same procedure as for **15** was employed using [PtCl₂(dppf)] (20 mg, 0.024 mmol), KS₂CNC₄H₆ (0.036 mmol), and NH₄PF₆ (8 mg, 0.049 mmol) to give a yellow product. Yield: 22 mg (88%). IR (solid state): 1632, 1523, 1482, 1453, 1436, 1354, 1307, 1265, 1169, 1098, 1035, 998, 929, 830 (ν_{PF}) cm⁻¹. ³¹P NMR (CDCl₃): 15.9 (s, dppf, $J_{PtP} = 3374$ Hz). ¹H NMR (CDCl₃): 4.42 (s, 4H + 4H, C₅H₄ + NCH₂); 4.61 (s, 4H, C₅H₄); 5.93 (s, 2H, HC=CH); 7.50-7.71 (m, 20H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 893 (100) [M]⁺. Anal. Calcd for C₃₉H₃₄F₆FeNP₃PtS₂ ($M_w = 1038.66$): C, 45.1; H, 3.3; N, 1.4. Found: C, 45.0; H, 3.4; N, 1.3.

 $[Ru(S_2CNC_4H_6)(dppm)_2]PF_6$ (17). (a) Compound 1 (40 mg, 0.034 mmol) and $[Ru(=CHPh)Cl_2(SIMes)(PCy_3)]$ (2.9 mg, 0.003 mmol) were dissolved in dry, degassed dichloromethane (20 mL), and the mixture was stirred for 24 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a colorless product, which was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 34 mg (86%).

(b) The same procedure as for **15** was employed using *cis*-[RuCl₂(dppm)₂] (20 mg, 0.021 mmol), KS₂CNC₄H₆ (0.032 mmol), and NH₄PF₆ (7 mg, 0.043 mmol) to give a colorless product. Yield: 19 mg (78%). IR (solid state): 1477, 1449, 1434, 1355, 1312, 1190, 1097, 1028, 999, 932, 835 (ν_{PF}) cm⁻¹. ³¹P NMR (d_6 -acetone): -19.5, -3.9 (t^v × 2, dppm, J_{HH} = 34.5 Hz). ¹H NMR (d_6 -acetone): 3.91, 4.36 (d × 2, 2 × 2H, NCH₂, J_{HH} = 14.9 Hz); 4.74, 4.35 (m × 2, 2 × 2H, PCH₂P); 5.96 (s, 2H, HC=CH); 6.71, 7.02, 7.20–7.39, 7.42–7.59, 7.90 (m × 5, 40H, C₆H₅) ppm. MS (ES positive): m/z (abundance) 1014 (100) [M]⁺. Anal. Calcd for C₅₅H₅₀F₆NP₅RuS₂ (M_w = 1159.05): C, 57.0; H, 4.4; N, 1.2. Found: C, 57.0; H, 4.3; N, 1.2.

 $[Ru(CH=CHC_6H_4Me-4)(S_2CNC_4H_6)(CO)(PPh_3)_2]$ (18). (a) Compound 3 (40 mg, 0.042 mmol) and $[Ru(=CHPh)Cl_2-(SIMes)(PCy_3)]$ (3.6 mg, 0.004 mmol) were dissolved in dry, degassed dichloromethane (20 mL), and the mixture was stirred for 24 h. All solvent was then removed, and the residue was triturated in diethyl ether (20 mL) to yield a colorless product, which was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 34 mg (88%).

(b) The same procedure as for **13** was employed using [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(CO)(PPh₃)₂] (20 mg, 0.021 mmol) and KS₂CNC₄H₆ (0.032 mmol) to give a colorless product. Yield: 10 mg (52%). IR (solid state): 1912 (ν_{CO}), 1477, 1355, 1266, 1185, 1032, 933, 851, 832 cm⁻¹. ³¹P NMR (CDCl₃): 39.5 (s, PPh₃). ¹H NMR (CDCl₃): 2.25 (s, 3H, CCH₃); 3.50, 3.77 (s(br) × 2, 2 × 2H, NCH₂); 5.58 (d, 1H, H^β, J_{HH} = 16.7 Hz); 5.62 (s, 2H, HC=CH); 6.45, 6.84 (AB, 4H, C₆H₄, J_{AB} = 7.9 Hz); 7.28-7.33, 7.57-7.62 (m × 2, 30H, C₆H₅); 7.77 (dt, 1H, Hα, J_{HH} = 16.7 Hz, J_{HP} = 3.2 Hz) ppm. MS (ES positive) *m*/*z* (abundance) 915 (8) [M]⁺; 798 (62) [M – alkenyl]⁺. Anal. Calcd for C₅₁H₄₅NOP₂RuS₂·CH₂Cl₂ (*M*_w = 999.99): C, 62.5; H, 4.7; N, 1.4. Found: C, 62.7; H, 4.7; N, 1.7.

Crystallography. Single crystals of complex **3** were grown by slow diffusion of ethanol into a dichloromethane solution of the compound.

Crystal Data for 3: [C₅₃H₄₉NOP₂RuS₂]·2CH₂Cl₂, $M_w = 1027.99$, triclinic, $P\overline{1}$ (No. 2), a = 11.9308(4) Å, b = 13.4909(4) Å, c = 17.5672(5) Å, $\alpha = 109.806(3)^\circ$, $\beta = 109.393(3)^\circ$, $\gamma = 93.684(2)^\circ$, V = 2459.09(15) Å³, Z = 2, $D_c = 1.388$ g cm⁻³, μ (Cu K α) = 5.290 mm⁻¹, T = 173 K, pale yellow needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 9569 independent measured reflections ($R_{int} = 0.0268$), F^2 refinement, R1-(obsd) = 0.0303, wR2(all) = 0.0807, 8384 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 145^\circ$), 583 parameters. CCDC 768226.

Single crystals of complex **5** were grown by slow diffusion of diethyl ether into a dichloromethane solution of the compound.

Crystal Data for 5: [C₃₄H₃₆NNiP₂S₂](PF₆)·C₄H₁₀O, $M_w = 862.50$, monoclinic, C2/c (No. 15), a = 21.0143(5) Å, b = 10.6307(3) Å, c = 36.8148(15) Å, $\beta = 97.725(3)^\circ$, V = 8149.7(5) Å³, Z = 8, $D_c = 1.406$ g cm⁻³, μ (Mo Kα) = 0.755 mm⁻¹, T = 173 K, orange blocks, Oxford Diffraction Xcalibur 3 diffractometer; 12 382 independent measured reflections ($R_{int} = 0.0324$), F^2 refinement, R1(obsd) = 0.1071, wR2(all) = 0.2567, 9319 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$), $2\theta_{max} = 64^\circ$), 469 parameters. CCDC 768227.

Single crystals of complex **15** were grown by slow diffusion of ethanol into a chloroform solution of the compound.

Crystal Data for 15: [C₃₂H₃₂NNiP₂S₂](PF₆)·1.75CHCl₃, $M_w = 969.22$, triclinic, PI (No. 2), a = 13.7545(4) Å, b = 15.2829(3) Å, c = 20.3044(4) Å, $\alpha = 92.0086(14)^\circ$, $\beta = 102.8560(19)^\circ$, $\gamma = 98.9786(18)^\circ$, V = 4099.38(17) Å³, Z = 4 (two independent complexes), $D_c = 1.570$ g cm⁻³, μ (Mo K α)=1.089 mm⁻¹, T = 173 K, orange prisms, Oxford Diffraction Xcalibur 3 diffractometer; 24 642 independent measured reflections ($R_{int} = 0.0173$), F^2 refinement, R1(obs)= 0.0381, wR2(all) = 0.0980, 16 353 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 64^\circ$), 1064 parameters. CCDC 768228.

The structures were refined using the SHELXTL and SHELX-97 program systems.³⁷ Further details can be found in the Supporting Information.

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Supporting Information Available: Text, figures, and CIF files giving crystallographic data for the structures of **3**, **5**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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