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Consecutive Insertion Reactions of Unsaturated Molecules into the Ni–C Bonds of the Nickelacycle $(\mathrm{Me_3P})_2\mathrm{Ni}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$. Formation of Heterocycles Derived from Seven-Membered Cyclic Acid Anhydrides

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$\mathrm{CS_2}$ inserts into the Ni–aryl bond of $(\mathrm{Me_3P})_2\mathrm{Ni}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$ (**1a**) at very low temperatures (−90 °C) with formation of $(\mathrm{Me_3P})_2\mathrm{Ni}(\eta^3\text{-}\mathrm{S_2CC_6H_4}\text{-}o\text{-}\mathrm{CMe_2CH_2})$ (**A**), which contains a Ni-η^3-*S,C,S′*-pseudoallylic moiety. Compound **A** spontaneously evolves at −70 °C to the dithiolactone complex $(\mathrm{Me_3P})_2\mathrm{Ni}(\eta^2\text{-}\mathrm{S{=}CSCH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$ (**3a**) by means of a reductive elimination process that involves C–S bond formation. Other heterocumulenes such as SCO, SCNPh, OCNPh, and $\mathrm{C(NC_6H_4}\text{-}p\text{-}\mathrm{Me)_2}$ also insert into the Ni–aryl bond of **1a**, but in these cases the resulting products are 16-electron species of composition $(\mathrm{Me_3P})_2\mathrm{Ni}(\mathrm{X\text{-}C({=}Y)C_6H_4}\text{-}o\text{-}\mathrm{CMe_2CH_2})$. When X ≠ Y, i.e., for unsymmetric heterocumulenes, the Ni center preferentially bonds to the softer heteroatom. All these seven-membered heterometallacycles undergo insertion into the Ni–$\mathrm{CH_2}$ linkage by reaction with CO or $\mathrm{CNBu^t}$ to afford products whose nature depends upon the particular, heterocumulene-derived functionality present in the starting complex. For instance, if a C=S group is available, Ni(0) species related to **3a**, e.g., $(\mathrm{Me_3P})_2\mathrm{Ni}(\eta^2\text{-}\mathrm{S{=}CSC({=}O)CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$ (**11a**), are formed. In the remaining cases, unusual eight-membered-ring Ni(II) η^2-iminoacyls, such as $(\mathrm{Me_3P})\mathrm{Ni}(\eta^2\text{-}\mathrm{C({=}NBu^t)CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4C({=}O)S})$ (**17**), or the free seven-membered heterocycles $\mathrm{O{=}C\text{-}X\text{-}C({=}Y)C_6H_4}\text{-}o\text{-}\mathrm{CMe_2CH_2}$ (along with $\mathrm{Ni(CO)_2(PMe_3)_2}$) are obtained when the entering reagent is $\mathrm{CNBu^t}$ or CO, respectively. Related organic heterocycles, derived from the parent seven-membered cyclic acid anhydride, can be readily obtained by further elaboration of the stable heteronickelacycles. The interaction of $\mathrm{CS_2}$ with the related nickelacycle $(\mathrm{dmpe})\mathrm{Ni}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$ (**1b**) (dmpe = $\mathrm{Me_2PCH_2CH_2PMe_2}$) takes a completely different course and yields the *gem*-dithiolate complex $(\mathrm{dmpe})\mathrm{Ni}(\mathrm{S_2CCH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4})$ (**4**), which is formally the product of the insertion of $\mathrm{CS_2}$ into the two Ni–C bonds of the starting nickelacycle. Compound **4** further reacts with $\mathrm{CS_2}$ to furnish the Ni(II) trithiocarbonate $(\mathrm{dmpe})\mathrm{Ni}(\eta^2\text{-}\mathrm{S_2C{=}S})$ (**5**) and the thioketone $\mathrm{S{=}CCH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4}$ (**6**). Complexes **3a**, **4**, and **5** have been characterized by single-crystal X-ray diffraction analyses. Crystallographic data: for **3a**, space group $P2_1/n$, $a = 19.847(8)$ Å, $b = 9.343(2)$ Å, $c = 13.939(3)$ Å, $\beta = 109.79(3)°$, $Z = 4$; for **4**, space group $Pbca$, $a = 11.888(4)$ Å, $b = 14.073(3)$ Å, $c = 25.065(3)$ Å, $Z = 8$; for **5**, space group $P2_1/n$, $a = 14.286(5)$ Å, $b = 7.486(1)$ Å, $c = 12.692(1)$ Å, $\beta = 93.40(2)°$, $Z = 4$.

Introduction

Recently, there has been increasing interest in the synthesis and reactivity of mononuclear complexes with sulfur-containing ligands, in part because of the reactivity they display toward organic substrates.[1] As a matter of fact, the applications of organosulfur chemistry in organic synthetic reactions have increased enormously in the last few years.[2] A useful synthetic approach to organotransition, organosulfur chemistry consists of the investigation of the reactivity of small, sulfur-containing molecules like $\mathrm{CS_2}$, COS, and RNCS with organometallic compounds.[3]

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(1) See: (a) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022. (b) Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (c) Liaw, W.-F.; Kim, C.; Darensbourg, M. Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 3591. (d) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (e) Seyferth, D.; Womack, G. B.; Archer, C. M.; Fackler, J. P.; Marler, D. O. *Organometallics* **1989**, *8*, 443. (f) Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 3465. (g) Jones, W. D.; Selmeczy, A. D. *Organometallics* **1992**, *11*, 889. (h) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613.

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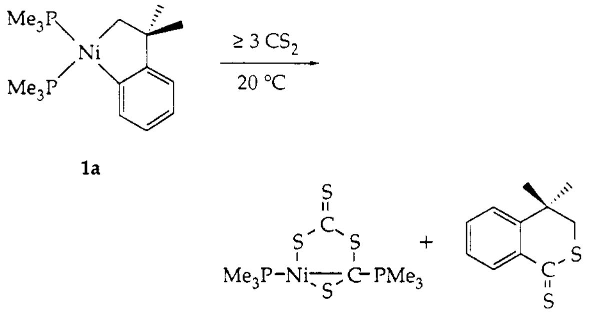
Metalacycles are organometallic species[4] of growing importance which are often involved in a number of catalytic reactions such as metathesis and dimerization of olefins, isomerization of strained organic cyclic compounds, cyclooligomerization of alkynes, and others.[5] In addition, their enhanced stability, as compared to metal alkyls, allows the study of some transformations of transition-metal compounds which undergo facile decomposition reactions. Despite the importance of metallacycles, some fundamental properties, in particular their insertion chemistry, remain far from being well understood.

In the intersection of these two areas of research, we have decided to investigate the insertion reactions of the sulfur-containing heterocumulenes CS_2, COS, and PhNCS with the nickelacycle[6,7] $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1a**) and other related species like the dmpe analog $(dmpe)Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1b**) (dmpe = $Me_2PCH_2CH_2PMe_2$). Here we provide a full account of these investigations, which include a related study of the reactivity of other heterocumulenes like PhNCO and $C(NC_6H_4\text{-}p\text{-}Me)_2$. Moreover, and taking advantage of the existence of two Ni–C bonds in **1a**, we have also investigated the successive insertions of the above heterocumulenes and other unsaturated molecules such as CO and $CNBu^t$. This has allowed the selective synthesis of a number of unusual seven-membered sulfur-containing heterocycles. Part of this work has been reported in preliminary form.[8]

Results

Reaction of 1a with CS_2. The nickelacycle **1a** has been shown to react only very slowly with CO_2,[6a] with formation of the nickelalactone complex $(PMe_3)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(=O)O)$, i.e., the product of the normal[9a] insertion of CO_2 into the Ni–aryl bond. A much faster and also more complex reaction ensues in the presence of CS_2. When an Et_2O solution of **1a** is treated with CS_2 (≥3 equiv) at 20 °C (eq 1), the heterometallacycle $Ni(C_2S_4PMe_3)(PMe_3)$, previously reported by Ibers,[10] separates as a red-brown microcrystalline solid. From the supernatant solution, the dark red crystalline dithiolactone **2** can be isolated by crystallization. Relevant spectroscopic features for **2** are an IR absorption at 1020 cm^{-1} due to $\nu(C{=}S)$ and a ^{13}C resonance at δ 224.7 attributable to the dithiolactone carbon, C(S)S.[11]

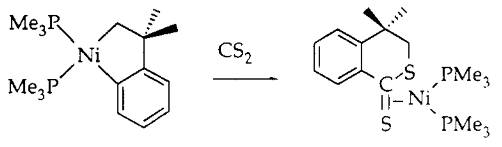


1a

2

(1)

In order to gain relevant mechanistic information about this interesting transformation, complex **1a** has been reacted with 1 equiv of CS_2 at −90 °C. A very dark green, almost black reaction mixture can be obtained that becomes red-orange in color on warming at −70 °C. No further changes are observed upon raising the temperature to 20 °C, and from the resulting solution the Ni(0) complex $(Me_3P)_2Ni(\eta^2\text{-}S{=}CC_6H_4\text{-}o\text{-}CMe_2CH_2S)$ (**3a**) crystallizes out (eq 2). At −70 °C, its $^{31}P\{^1H\}$ NMR spectrum shows an AX pattern ($\delta_A = -8.4$, $\delta_X = -7.1$) with a small cisoid coupling of 7 Hz. The higher field signal further splits by coupling to the $^{13}C(S)S$ carbon in the spectrum of **3a*** (50% $^{13}CS_2$-enriched[9b]). The value of this coupling (33 Hz) can also be computed from the ^{13}C resonance of the dithiolactone carbon, which appears as a doublet at δ 58. The very high-field chemical shift of this signal and the large $^2J_{CP}$ value found are in favor of the η^2-coordination mode proposed for the dithiolactone ligand which has been confirmed by X-ray studies (see below).



1a 3a

(2)

The nature of the products formed in the transformations represented in eqs 1 and 2 suggests that the reaction of **1a** with CS_2 occurs with insertion into the Ni–aryl bond to give an unstable, dark green intermediate **A**, which spontaneously undergoes reductive elimination with for-

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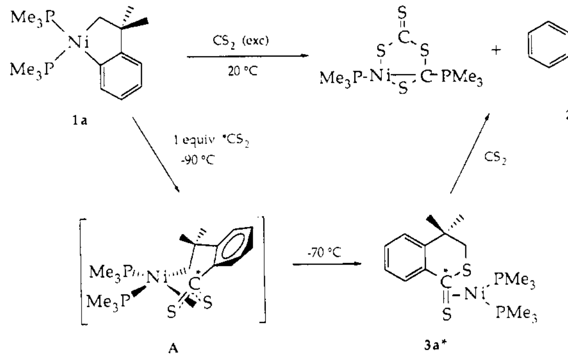
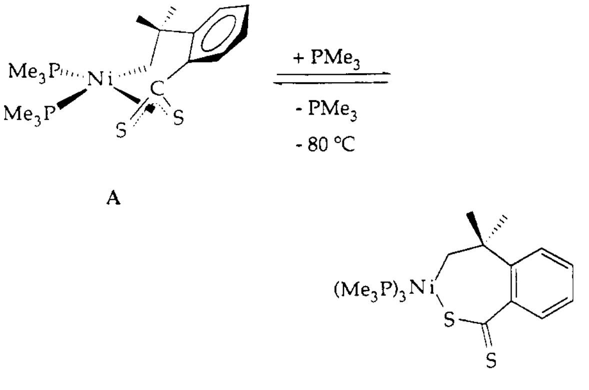
Scheme 1



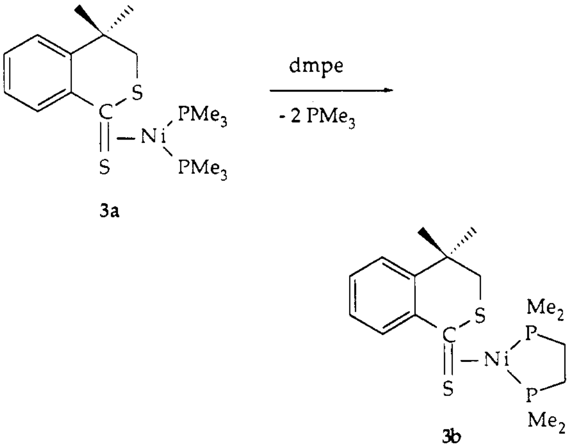
mation of the dithiolactone complex **3a**. If additional amounts of CS$_2$ are present, displacement of the organic fragment and head-to-tail dimerization of two molecules of CS$_2$ take place, yielding Ibers's complex and the free dithiolactone **2**. In accord with this, the reaction of **3a*** with CS$_2$ gives **2*** and Ibers's complex with normal isotopic composition. Scheme 1 summarizes these results. As for the nature of **A**, we propose its formulation as containing an η^3-*S,C,S'*-dithiocarboxylate moiety.[12a] This is based mainly on the observation of a doublet at 137 ppm for the -CS$_2$ carbon ($^2J_{CP}$ = 19 Hz) in the ^{13}C NMR spectrum of a solution obtained upon mixing equimolar amounts of **1a** and ^{13}CS$_2$ at -90 °C. This signal appears at much higher field than expected for η^1-*S*- or η^2-*S,S'*-bonded dithiocarboxylate ligands[12b–e] but in the same region found for structurally characterized Mo, Fe, and Ru complexes that exhibit this unusual η^3-pseudoallylic bonding mode.[12d,13,14] Other spectroscopic data, including the $^1J_{CC}$ value of 55 Hz[15] found for the quaternary aromatic carbon adjacent to the *CS$_2$ group, are in agreement with the proposed structure.

Interestingly, intermediate **A** reacts reversibly with PMe$_3$ at -80 °C to give the brown tris(phosphine) species **B** shown in eq 3. A large excess of PMe$_3$ is needed to completely shift the equilibrium toward the formation of **B**. This species displays an AMX spin pattern in the ^{31}P{^{1}H} NMR spectrum and a singlet at δ 258 in the ^{13}C{^{1}H} NMR spectrum (sample enriched in ^{13}CS$_2$). The latter is in the range found for other η^1-S$_2$CR ligands.[12b] At higher temperatures, **B** becomes fluxional, and at -60 °C, it transforms into the dithiolactone complex **3a**.



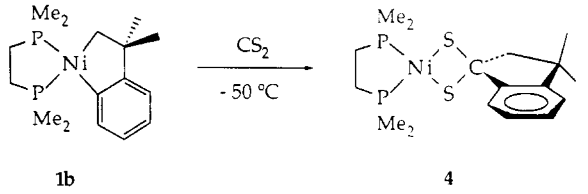
(3)

Action of carbon monoxide on **3a** also liberates the dithiolactone **2** and forms Ni(CO)$_2$(PMe$_3$)$_2$. With dmpe, however, the related complex **3b** (eq 4) is formed.



(4)

Reaction of 1b with CS$_2$. Rather unexpectedly, the reaction of **1b** with CS$_2$ takes a very different course. Mixing together equimolar quantities of **1b** and CS$_2$ at room temperature generates the orange 1,1-dithiolate complex **4** (eq 5). Monitoring the reaction by ^{31}P{^{1}H} NMR spectroscopy shows that **4** starts forming at temperatures near -50 °C without any detectable intermediates. Support for this structure comes from spectroscopic studies and from an X-ray determination (see below). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4** reflect the existence of a plane of symmetry. Thus, the two CH$_2$PMe$_2$ units give rise to a single set of resonances, and enantiotopic CH$_2$ protons and CMe$_2$ methyls are observed. The ^{13}C{^{1}H} spectrum of **4*** [9b] shows a singlet at δ 66.2 due to the CS$_2$ carbon of the 1,1-dithiolate ligand. This is in the region found for other complexes of this type,[1a,g,16] e.g., 63.3 ppm in Fe$_2$(CO)$_6$(μ_2-S$_2$CH$_2$)[16a] and 54 ppm in Cp*Rh(S$_2$CH$_2$)-



(5)

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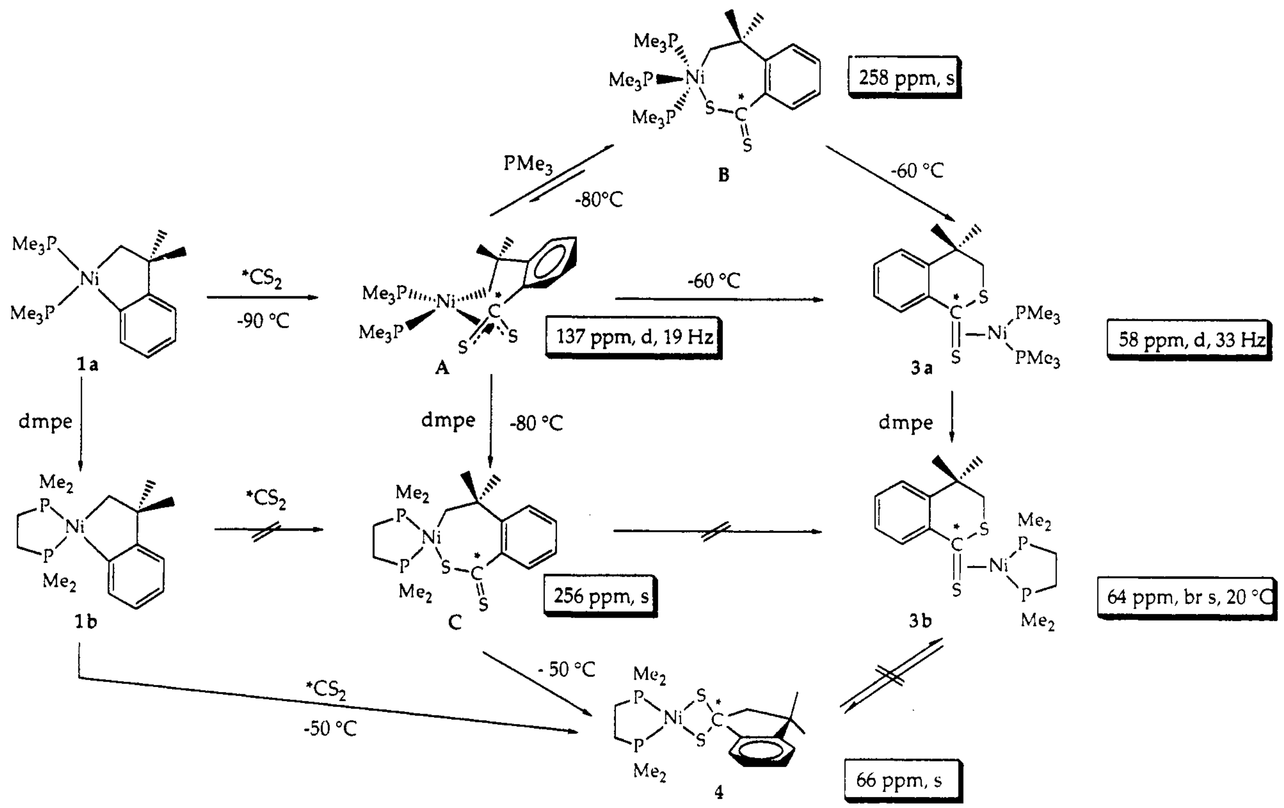
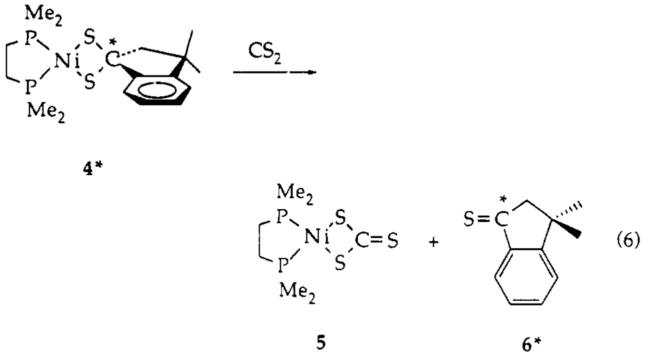
Scheme 2



(PMe$_3$).[1g] On the other hand, the methylene and one of the aromatic quaternary carbons of the original neophyl ligand, now bonded to the *CS$_2$ unit, display $^1J_{CC}$ couplings of 36 and 45 Hz, respectively.

Although complexes **3b** and **4** are isomers, no interconversion between them can be observed under normal conditions (Scheme 2). An alternative reaction pathway to **4** is by the **A** → **C** → **4** route depicted in Scheme 2, which summarizes all the already described experimental findings as well as the $^{13}CS_2$ NMR data (δ and J_{CP}). Thus, treatment of **A** (generated at −90 °C from **1a** and 1 equiv of CS$_2$) with dmpe at −80 °C furnishes the *S*-bonded dithiocarboxylate complex **C** which spontaneously reorganizes to **4** at temperatures above −50 °C by C–C bond formation and complexation of the uncoordinated sulfur. Once again, the change in the coordination mode of the -CS$_2$ moiety from η^3 to η^1 is accompanied by a shift in the corresponding ^{13}C resonance from 137 to 256 ppm. Competition experiments using equimolar mixtures of **1b** + CS$_2$ and **C** show that the former converts to **4** at a faster rate than **C**. *This and the fact that no intermediates are observed in the reaction of* **1b** *and CS$_2$ indicates that* **C** *cannot be an intermediate in the* **1b** → **4** *transformation.*

Interestingly, the 1,1-dithiolate **4** reacts with additional amounts of CS$_2$, with formation of the crystalline trithiocarbonate[17] **5** (structurally characterized by X-ray crystallography, see below) and the thioketone **6** (eq 6), isolated as a violet, distillable oil.[18,19] Isotopic labeling studies using **4*** demonstrate that the bridging carbon of the heterospirocycle becomes incorporated exclusively into the cyclic thioketone. Other reagents such as Br$_2$ and HCl also cleave the CS$_2$ moiety of **4** and generate the thioketone **6**. In addition, NiBr$_2$(dmpe) plus sulfur and NiCl$_2$(dmpe) plus H$_2$S are respectively formed.[20]



To complete these studies, the reaction of the 2,2′-bipyridine complex (bipy)Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$) (**1c**) and CS$_2$ has been studied. Compound **1c** can be prepared by the simple ligand displacement reaction of eq 7 and has been fully characterized by conventional analytical and spectroscopic techniques (see Experimental Section). Its

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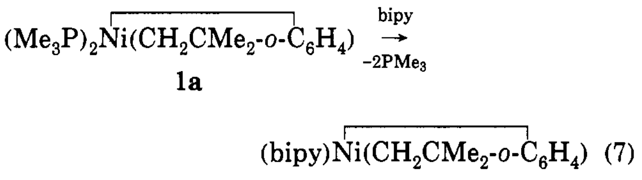
[17] Trithiocarbonate complexes can adopt a variety of bonding schemes. Some recent examples include the following. η^2-S$_2$C=S: (a) Bianchini, C.; Meli, A.; Vizza, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 767. μ_2-η^2,η^2-S$_2$C=S: ref 14a. μ_4-S$_2$C=S: (b) Lanfredi, A. M. M.; Tiripicchio, A.; Camus, A.; Marsich, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1126. For some η^2-trithiocarbonate complexes of Ni, see: (c) Burke, J. M.; Fackler, J. P., Jr. *Inorg. Chem.* **1972**, *11*, 2744. (d) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1982**, 799.

[18] Many thioketones such as Me$_2$C=S are unstable molecules that can be stabilized only by complexation to transition-metal centers. See: (a) Gingerich, R. G W.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *132*, 377. (b) Karcher, B. A.; Jacobson, R. A. *J. Organomet. Chem.* **1977**, *132*, 387. (c) Wang, S.; Fackler, J. P., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 22.

[19] Aryl-substituted thioketones are normally isolable compounds. For the related, fully methylated thioketone CMe$_2$CMe$_2$-*o*-C$_6$H$_4$C=S, see: Klages, C.-P.; Voss, J. *Chem. Ber.* **1980**, *113*, 2255.

[20] The reaction with HCl probably affords the corresponding free *gem*-dithiol that immediately decomposes to the thioketone and SH$_2$. See: Mayer, R.; Hiller, G.; Nitzschke, M.; Jentzsch, J. *Angew. Chem.* **1963**, *75*, 1011.

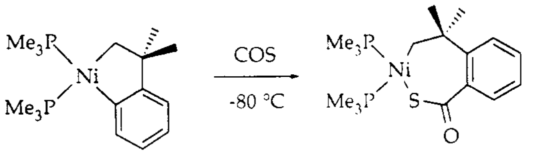


$$(\mathrm{Me_3P})_2\mathrm{Ni(CH_2CMe_2\text{-}\mathit{o}\text{-}C_6H_4)} \xrightarrow[-2\mathrm{PMe_3}]{\mathrm{bipy}} (\mathrm{bipy})\mathrm{Ni(CH_2CMe_2\text{-}\mathit{o}\text{-}C_6H_4)} \quad (7)$$

1a **1c**

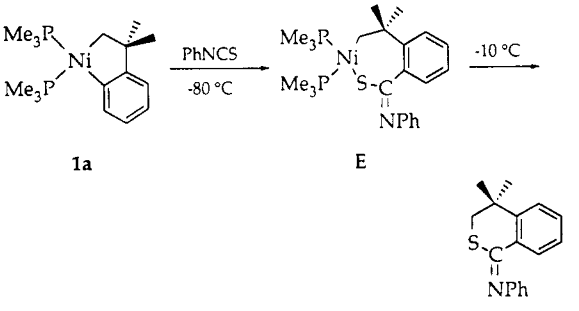
interaction with an excess of CS_2 gives the dithiolactone **2** together with an insoluble brown precipitate. Although the reproducibility of this reaction is rather poor, the brown solid can be shown by IR spectroscopy to contain (bipy)-Ni(η^2-CS_2),[21] but this system was not investigated any further.

Reactions of 1a with COS, PhNCS, PhNCO, and C(NC$_6$H$_4$-*p*-Me)$_2$. Carbonyl sulfide and **1a** react very fast, even at −80 °C, to afford a dark red solution of the insertion product **D** (eq 8). Compound **D** is an unstable species that decomposes upon warming at 20 °C to yield a complex mixture of compounds that has not been further investigated. Formulation **D** is proposed on the basis of the characteristic insertion chemistry of this species, to be described in the following sections, and also on the basis of its similarity with other related metallacycles reported in this contribution.



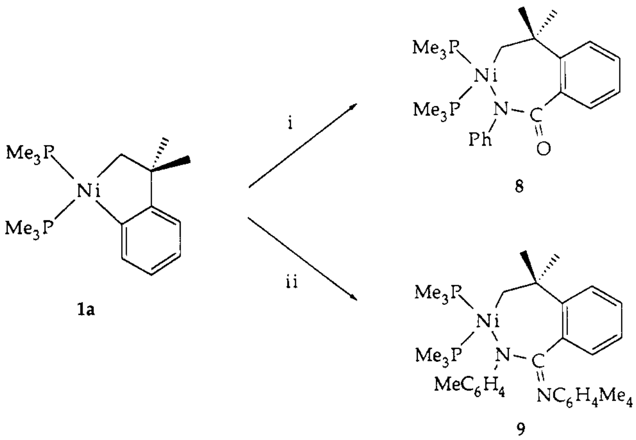
1a D (8)

PhNCS also reacts quickly with **1a** at −80 °C (eq 9) to provide the heterometallacycle **E**, which can be isolated as a crystalline solid at low temperatures. This species decomposes at −10 °C, both in solution and in the solid state, to give the cyclic imine thioether **7**. Important spectroscopic data for **E** include a doublet of doublets at δ 33.7 in the $^{13}C\{^1H\}$ NMR spectrum ($^2J_{CP}$ = 68 and 21 Hz) due to the methylene carbon and a doublet at δ 179.7 ($^3J_{CP}$ = 12 Hz) for the imine carbon. When the above reaction is effected in the presence of excess PMe_3 (3–4 equiv), a related species **F**, containing three coordinated PMe_3 ligands, is formed. **F** can also be obtained directly from **E** and PMe_3. Its $^{13}C\{^1H\}$ NMR spectrum indicates that the heterometallacycle remains unaltered, while its $^{31}P\{^1H\}$ spectrum reveals an AMX spin pattern. As for other related systems reported in this work, the **E**→**F** conversion is presumably reversible, but the low stability of both species has prevented a more detailed study.



1a E 7 (9)

Scheme 3[a]



[a] (i) PhNCO; (ii) C(NC$_6$H$_4$-*p*-Me)$_2$.

More stable insertion products result from the reactions of **1a** with phenyl isocyanate[22] and *p*-tolylcarbodiimide (Scheme 3). Compounds **8** and **9** are stable, crystalline species that can be heated at 50–60 °C without noticeable decomposition. The spectroscopic data collected in the Experimental Section are in accord with the proposed structures and require no further comments. We note, however, that two isomers, (*N*- or *O*-bonded) are possible for **8**, of which the Ni–N isomer[23] is strongly favored by a careful comparison of the lower-field region of the $^{13}C\{^1H\}$ NMR spectra of **8** and **9**. In particular, the signal at δ 159 in the spectrum of **9**, which can be safely assigned to the *C*=NAr group, is absent in the spectrum of **8**, which, in turn, exhibits a resonance at 171 ppm, in accord with the existence of a >C=O functionality.

The reaction leading to **8** can be monitored by low-temperature NMR spectroscopy. The formation of **8** at a convenient rate starts only at −60 °C, with no intermediates being detected. The presence of added PMe_3 (4 equiv) slows down the insertion reaction, but at −30 °C a tris(PMe_3) complex **G** (analogous, for example, to **F**) forms. In this case, **G** can be reversibly converted to **8** by simple removal of the volatiles *in vacuo*.

Reactivity of 1a–c toward CO and CNBu^t. The room temperature reaction of **1a** with CO has been shown[6a] to provide the products of the right-hand side of eq 10. Carrying out the reaction at −70 °C introduces no changes, and, moreover, we have been unable to characterize spectroscopically the proposed intermediate **H**. Nevertheless, evidence for the precise site of the insertion can be gained from the successive incorporation of CO and CS_2 (in either order), to be discussed below (see Scheme 4).

The dmpe derivative **1b** exhibits a more interesting behavior, and at −80 °C, under a CO atmosphere, the characteristic AX spin pattern of its $^{31}P\{^1H\}$ NMR spectrum collapses into a broad singlet that persists until temperatures close to 0 °C. Bubbling CO at 20 °C for 5–10 min induces insertion with formation of Ni(CO)$_2$-(dmpe) and the above cyclic ketone. Since the $^{31}P\{^1H\}$

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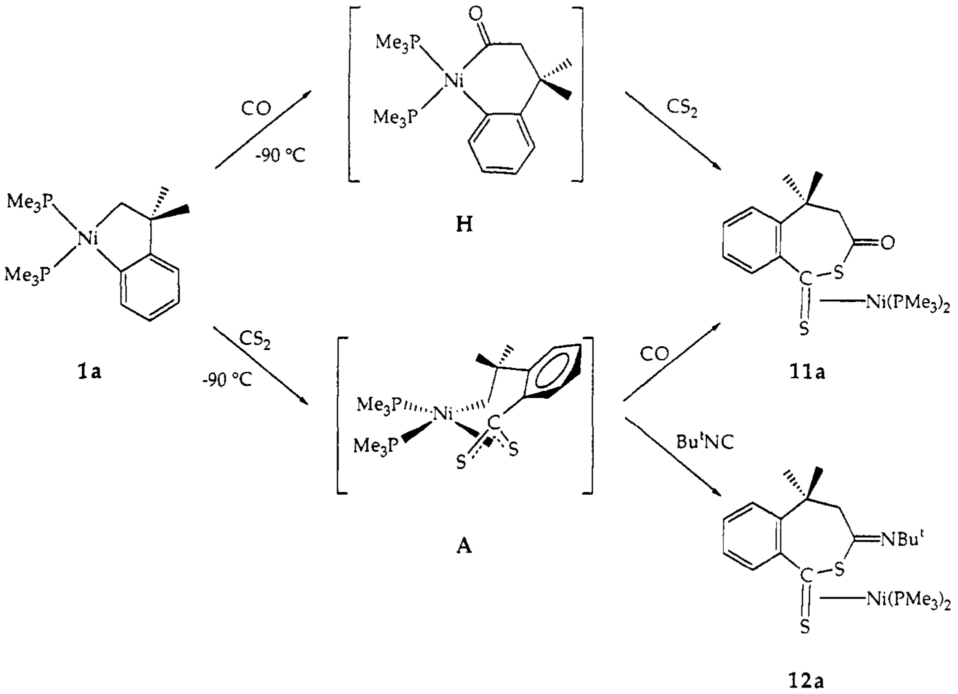
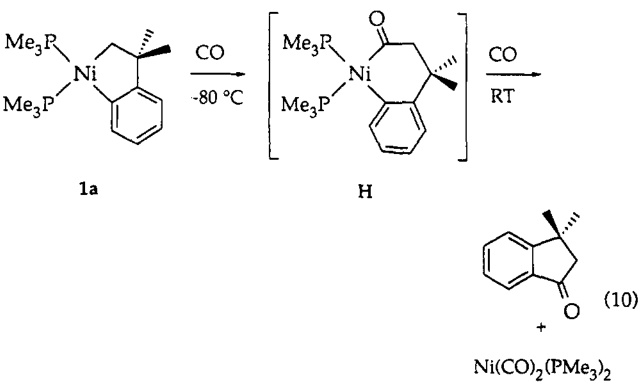
[21] Uhlig, E.; Poppitz, W. *Z. Chem.* **1975**, *19*, 191.

[22] See: Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927 for a recent review on transition metal–isocyanate chemistry.

[23] Other synthetic routes are available for the formation of this kind of heterometallacycle. See: (a) Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448. (b) Hoberg, H.; Hernández, E. *J. Chem. Soc., Chem. Commun.* **1986**, 544. The same selectivity upon insertion is observed by Ti(III) alkyls. See: Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297.

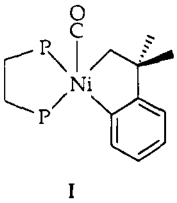
Scheme 4





(10)

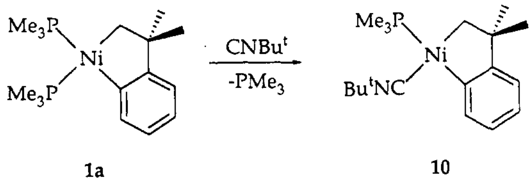
spectrum of solutions of **1b** + CO at low temperatures is only slightly displaced from the center of gravity of the AX system, it can be proposed both that this behavior is due to the achievement of an equilibrium between **1b** and the fluxional,[24] 5-coordinate adduct **I** and that this equilibrium favors the starting complex **1b**. Finally, in



I

this respect, no reaction is observed between complex **1c** and CO, even after prolonged exposures of solutions of **1c** to this gas (20 °C, 2 atm, 10 h). Interestingly, the bipy ligand of **1c** is instantaneously displaced by dmpe at −80 °C to yield **1b**. Hence, the relative stabilities of metalacycles **1a–c** follow the order **1b** > **1c** > **1a** (i.e., dmpe > bipy > PMe$_3$).

Complex **1a** reacts with CNBu^t under ambient conditions (eq 11) to give the mixed adduct $(Me_3P)(Bu^tNC)\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)}$ (**10**). Isocyanide insertion is not



(11)

observed, even after prolonged heating at 60 °C. The formation of **10** clearly reflects the higher trans effect of the Ni–alkyl bond as compared with the Ni–aryl moiety, and it is closely reminiscent of that of the analogous pyridine derivative $(Me_3P)(py)\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)}$.[6b] Low-temperature NMR studies of solutions of **1b** + CNBu^t show evidence for the formation of the adduct **1b·CNBu^t**, analogous to **I**. This seems to be strongly favored at low temperatures, but the system does not evolve any further.

Successive Insertions of the Heterocumulenes X=C=Y and CO or CNBu^t into the Ni—C Bonds of 1a. Formation of Seven-Membered Sulfur-Containing Heterocycles. Treatment of *in situ* formed **A** (Scheme 4) with an excess of CO yields an orange crystalline compound **11a** as a result of CO insertion followed by reductive elimination. The proposed coordination of the acyl thioacyl sulfide functionality is similar to that of the dithiolactone ligand in complex **3**, and it is based on similar spectroscopic arguments, particularly the observation of a doublet at 65 ppm ($^2J_{CP}$ = 27 Hz) for the labeled carbon in the $^{13}C\{^1H\}$ spectrum of a sample of **11a***. The C=O bond gives rise to an IR absorption at 1650 cm^{-1} and to a characteristic ^{13}C resonance at 208 ppm, i.e., in the region expected for a thioester, -SC(=O)-, moiety.[11]

As shown in Scheme 4, complex **11a** can also be obtained by carrying out the reaction in the reverse order. This unambiguously demonstrates that CO regioselectively inserts into the Ni–alkyl bond and that the resulting

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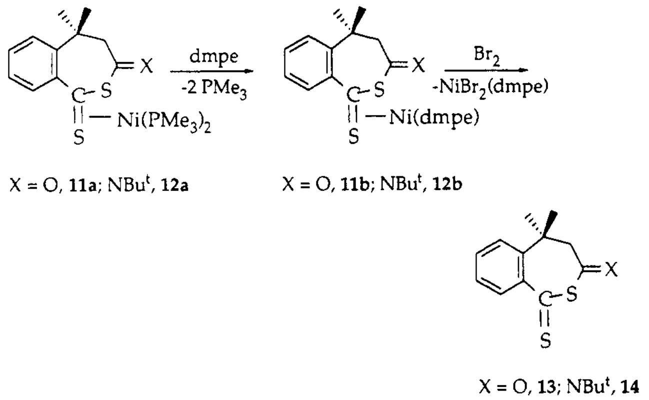
[24] The pentacoordinate species $(Ph_3P)_3\overline{Ni(CH_2CH_2CH_2CH_2)}$ has been reported to be highly fluxional even at low temperatures. See: Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418.

Scheme 5

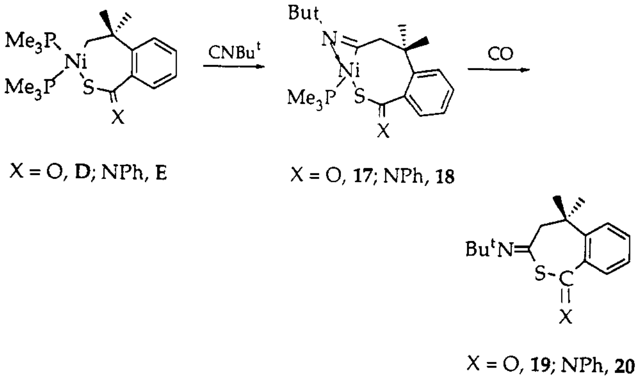


X = O, **11a**; NBu^t, **12a**

X = O, **11b**; NBu^t, **12b**

X = O, **13**; NBu^t, **14**

Scheme 6



X = O, **D**; NPh, **E**

X = O, **17**; NPh, **18**

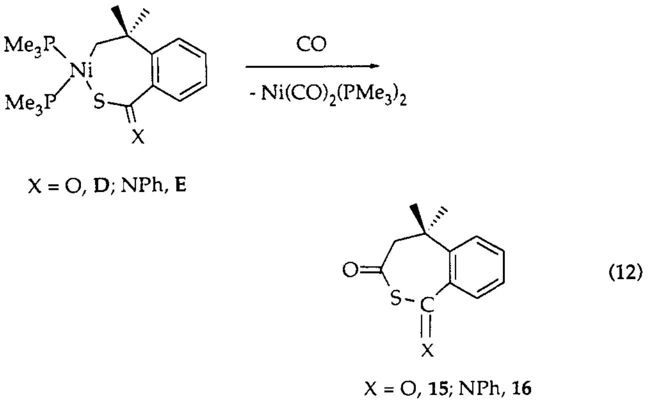
X = O, **19**; NPh, **20**

intermediate, **H**, undergoes CS$_2$ insertion into the Ni–aryl bond at a faster rate than reductive elimination.

The analogous reaction of **A** with CNBu^t (Scheme 4) yields complex **12a**, which contains an imine thioacyl sulfide ligand. It seems likely that prior to the formation of **11a** and **12a**, unstable acyl dithiocarboxylate and iminoacyl dithiocarboxylate intermediates, respectively, are produced and that these species undergo fast reductive elimination to afford the final products.

Displacement of the PMe$_3$ ligands in **11a** and **12a** by Me$_2$PCH$_2$CH$_2$PMe$_2$ gives the corresponding dmpe derivatives **11b** and **12b**, respectively (Scheme 5), which prove to be suitable starting products for the liberation of the organic ligands **13** and **14**, respectively.[25] As shown in Scheme 5, treatment with Br$_2$ gives the desired compounds together with NiBr$_2$(dmpe). Salient spectroscopic features for **13** and **14** are given in the Experimental Section.

The COS- and PhNCS-derived heterometalacycles, **D** and **E**, respectively, behave somewhat differently in their reactions with CO and CNBu^t. In the case of CO, the organic fragment resulting from the reductive elimination (following insertion) no longer remains coordinated to Ni under the reaction conditions[26] and can be directly obtained from the reaction mixture (eq 12). By contrast, the analogous reactions with CNBu^t provides unusual, albeit isolable, organometallic complexes containing eight-membered heterometalacycles and an η^2-iminoacyl functionality[27a] (Scheme 6). The Ni–η^2-iminoacyl linkage[27b] is characterized by ν(C=N) at 1720 cm^{-1} and δ(C=N) at 176 ppm (doublet, $^2J_{CP}$ = 63 Hz). The large $^2J_{CP}$ value is clearly indicative of a trans C–Ni–P arrangement. The acyl imine sulfide **19** and the bis(imine) sulfide **20** can be obtained in excellent yields by treatment of **17** and **18**, respectively, with CO.[26]

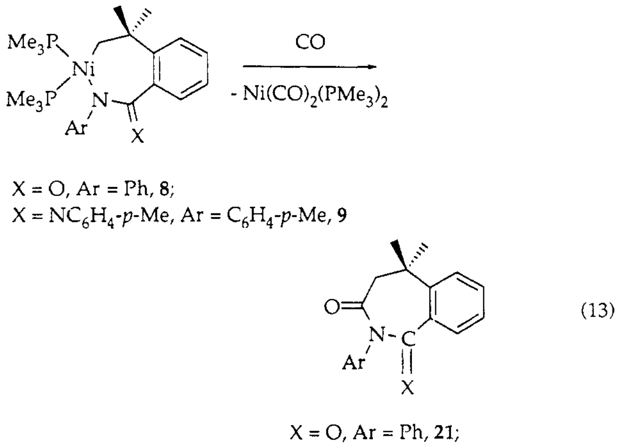


X = O, **D**; NPh, **E**

(12)

X = O, **15**; NPh, **16**

Finally, we have investigated the reactions of the thermally stable heterometallacycles **8** and **9** with CO and CNBu^t. While in the latter case a clean reaction could not be induced, the addition of CO to **8** and **9** evolves as depicted in eq 13 and affords the bis(acyl) amine **21** and the acyl amidine **22** in good yields.[28] The proper characterization of the PhNCO-derived product **21** is of particular importance as a further test for the proposed regiochemistry of the insertion of PhNCO in **1a**. Since **22** has been unambiguously characterized, a comparison of the ^{13}C{^{1}H} NMR spectra of both compounds seems pertinent to this aim. While **22** shows two resonances at 157 and 168 ppm, attributable to the C=N and CO functionalities, two very close resonances (δ 174 and 176) are observed for **21**, in agreement with the existence of two carbonyl groups.



X = O, Ar = Ph, **8**;
X = NC$_6$H$_4$-*p*-Me, Ar = C$_6$H$_4$-*p*-Me, **9**

(13)

X = O, Ar = Ph, **21**;
X = NC$_6$H$_4$-*p*-Me, Ar = C$_6$H$_4$-*p*-Me, **22**

X-ray Studies of Complexes 3a, 4, and 5. The solid-state structures of the dithiolactone complex **3a**, the 1,1-

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[25] For thio derivatives of acid anhydrides, see: (a) Kato, S.; Katada, T.; Mizuta, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 766. (b) Kato, S.; Sugino, K.; Yameda, M.; Katada, T.; Mizuta, M. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 879. (c) Kato, S.; Sugino, K.; Mizuta, M.; Katada, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 675. (d) Lakshmikantham, M. V.; Carroll, P.; Furst, G.; Levinson, M. I.; Cava, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 6084. (e) Yoneda, S.; Ozaki, K.; Yanagi, K.; Minobe, M. *J. Chem. Soc., Chem. Commun.* **1986**, 19.

[26] Carbon monoxide is known to promote reductive elimination in closely related systems. See: (a) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1981**, 193. (b) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (c) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Organomet. Chem.* **1987**, *332*, 345.

[27] (a) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (b) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583.

[28] For a related reaction, see ref 23a.

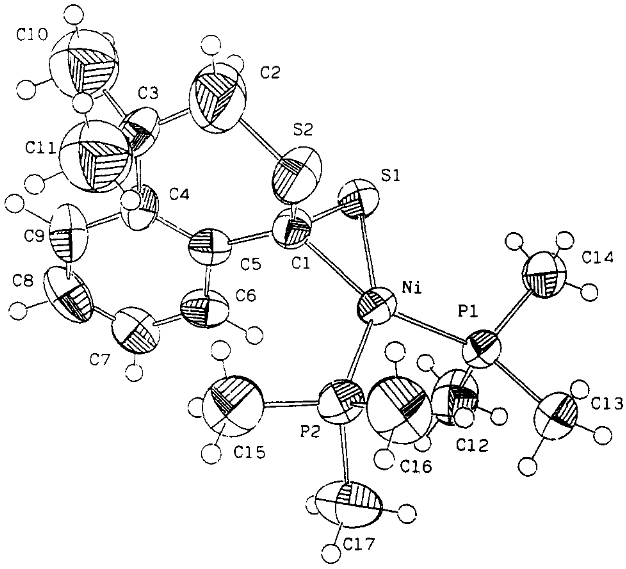

Figure 1. ORTEP view and atom labeling scheme of compound **3a**.

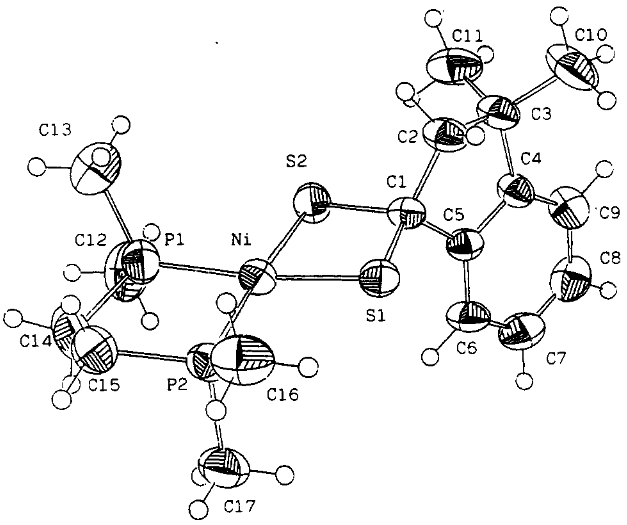

Figure 2. ORTEP view and atom labeling scheme of compound **4**.

dithiolate **4**, and the trithiocarbonate **5** have been determined and are illustrated by ORTEP plots in Figures 1–3. Tables 1–3 collect important bond distances and angles, and Table 4 gives a summary of the crystallographic data for the three compounds.

The molecules of **3a** contain formally three-coordinated Ni(0), bonded to two PMe$_3$ groups and to the C=S bond of the dithiolactone ligand, which is considered to occupy a single coordination site (the bite angle of the >C=S entity is very acute, 51.2(3)°). The two trimethylphosphine ligands have normal bond lengths and angles, and the triatomic NiCS linkage displays bonding parameters similar to those found in complexes that contain η^2-thioketone,[18,29,30] -thioketene,[31] and related ligands. Thus, the coordinated C—S bond distance (C1—S1, 1.77(1) Å) is essentially identical with the values of 1.769(2) and 1.762(4) Å found respectively in Mo[29] and V[30] thioketone

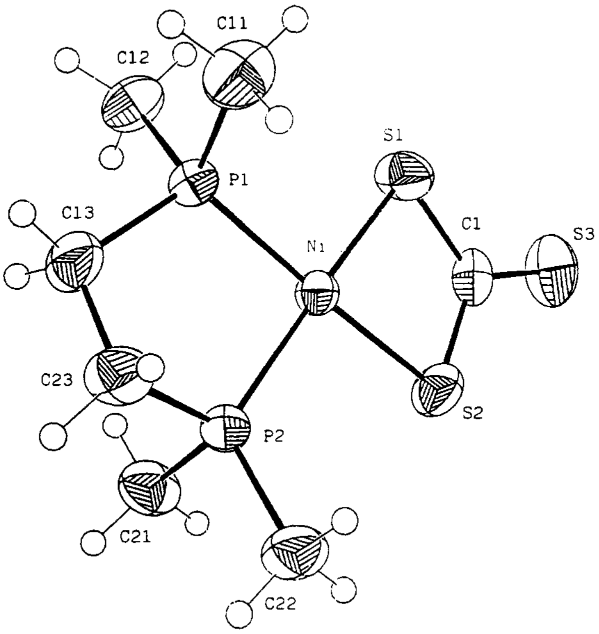

Figure 3. ORTEP view and atom labeling scheme of compound **5**.

Table 1. Bond Distances (Å) and Angles (deg) for 3a

	Distances		
Ni–P1	2.181(4)	S2–C2	1.82(2)
Ni–P2	2.146(3)	C1–C5	1.50(1)
Ni–S1	2.130(3)	C2–C3	1.43(2)
Ni–C1	1.94(1)	C3–C4	1.54(1)
P1–C12	1.80(1)	C3–C10	1.48(2)
P1–C13	1.82(1)	C3–C11	1.52(2)
P1–C14	1.81(1)	C4–C5	1.39(2)
P2–C15	1.82(2)	C4–C9	1.39(1)
P2–C16	1.80(2)	C5–C6	1.41(1)
P2–C17	1.81(1)	C6–C7	1.38(1)
S1–C1	1.77(1)	C7–C8	1.35(2)
S2–C1	1.78(1)	C8–C9	1.37(2)
	Angles		
S1–Ni–C1	51.2(3)	Ni–C1–S2	110.6(5)
P2–Ni–C1	101.4(3)	Ni–C1–S1	70.0(4)
P2–Ni–S1	152.5(2)	S2–C1–C5	114.7(6)
P1–Ni–C1	152.8(3)	S1–C1–C5	117.0(6)
P1–Ni–S1	101.7(1)	Ni–C1–C5	120.8(6)
P1–Ni–P2	105.7(1)	C2–C3–C11	106(1)
Ni–P1–C14	114.5(4)	C2–C3–C10	109(1)
Ni–P1–C13	123.9(4)	C2–C3–C4	115(1)
Ni–P1–C12	111.2(4)	C10–C3–C11	104(1)
C13–P1–C14	99.2(6)	C4–C3–C11	109(1)
C12–P1–C14	103.3(6)	C4–C3–C10	113(1)
C12–P1–C13	102.2(6)	C3–C4–C9	119.0(9)
Ni–P2–C17	116.3(4)	C3–C4–C5	122.5(8)
Ni–P2–C16	115.6(5)	C5–C4–C9	118.6(9)
Ni–P2–C15	119.7(5)	C1–C5–C4	124.8(8)
C16–P2–C17	102.9(6)	C4–C5–C6	118.8(9)
C15–P2–C17	99.3(6)	C1–C5–C6	116.4(8)
C15–P2–C16	100.3(6)	C5–C6–C7	121.0(9)
Ni–S1–C1	58.8(3)	C6–C7–C8	120(1)
C1–S2–C2	95.4(6)	C7–C8–C9	121(1)
S1–C1–S2	116.5(6)	C4–C9–C8	123(1)

compounds and with that of 1.744(3) Å characteristic of the thioformaldehyde derivative Cp$_2$Ti(η^2-SCH$_2$)(PMe$_3$).[32] This C1—S1 bond separation in complex **3a**, although intermediate between typical C=S and C—S lengths (1.70 and 1.82 Å, respectively) approaches the single bond limit (compare, for example, with the single C2—S2 bond of 1.82(2) Å) as a reflection of a strong bonding interaction between the metal center and the coordinated C=S

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(29) Alper, H.; Silvawe, N. D.; Birnbaum, G.; Ahmed, F. *J. Am. Chem. Soc.* **1979**, *101*, 6582.

(30) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Villa, A.; Gaustini, G. *Inorg. Chem.* **1983**, *22*, 841.

(31) Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1985**, *118*, 873.

(32) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650.

Table 2. Bond Distances (Å) and Angles (deg) for 4

	Distances		
Ni–P1	2.150(2)	C1–C5	1.499(6)
Ni–P2	2.148(1)	C2–C3	1.543(6)
Ni–S1	2.170(1)	C3–C4	1.515(6)
Ni–S2	2.170(1)	C3–C10	1.524(7)
P1–C12	1.797(3)	C3–C11	1.532(7)
P1–C13	1.798(6)	C4–C5	1.380(6)
P1–C14	1.833(6)	C4–C9	1.390(6)
P2–C15	1.830(5)	C5–C6	1.387(6)
P2–C16	1.796(5)	C6–C7	1.378(7)
P2–C17	1.809(5)	C7–C8	1.375(7)
S1–C1	1.831(4)	C8–C9	1.397(7)
S2–C1	1.848(4)	C14–C15	1.512(8)
C1–C2	1.534(4)		
	Angles		
S1–Ni–S2	80.12(6)	S1–C1–C5	116.2(3)
P2–Ni–S2	175.23(7)	S1–C1–C2	114.0(3)
P2–Ni–S1	95.79(5)	C2–C1–C5	101.4(3)
P1–Ni–S2	96.59(6)	C1–C2–C3	107.6(3)
P1–Ni–S1	173.37(6)	C2–C3–C11	111.4(4)
P1–Ni–P2	87.74(6)	C2–C3–C10	112.7(4)
Ni–P1–C14	108.9(2)	C2–C3–C4	100.6(4)
Ni–P1–C13	113.7(2)	C10–C3–C11	109.3(4)
Ni–P1–C12	120.6(2)	C4–C3–C11	109.3(4)
C13–P1–C14	103.5(3)	C4–C3–C10	113.2(4)
C12–P1–C14	105.3(3)	C3–C4–C9	128.3(4)
C12–P1–C13	103.3(3)	C3–C4–C5	111.1(4)
Ni–P2–C17	114.3(2)	C5–C4–C9	120.5(4)
Ni–P2–C16	118.4(2)	C1–C5–C4	111.8(4)
Ni–P2–C15	108.9(2)	C4–C5–C6	120.4(4)
C16–P2–C17	103.7(3)	C1–C5–C6	127.8(4)
C15–P2–C17	104.2(3)	C5–C6–C7	119.3(4)
C15–P2–C16	106.1(3)	C6–C7–C8	120.7(5)
Ni–S1–C1	90.8(1)	C7–C8–C9	120.5(5)
Ni–S2–C1	90.3(1)	C4–C9–C8	118.6(4)
S1–C1–S2	98.8(2)	P1–C14–C15	109.3(4)
S2–C1–C5	112.3(3)	P2–C15–C14	107.6(4)
S2–C1–C2	115.0(3)		

Table 3. Bond Distances (Å) and Angles (deg) for 5

	Distances		
Ni–P1	2.148(1)	C13–C23	1.532(7)
Ni–P2	2.141(1)	P1–C11	1.809(6)
Ni–S1	2.198(2)	P1–C12	1.798(5)
Ni–S2	2.195(2)	P1–C13	1.819(6)
S1–C1	1.722(5)	P2–C21	1.805(5)
S2–C1	1.725(5)	P2–C22	1.811(5)
S3–C1	1.648(5)	P2–C23	1.816(6)
	Angles		
S1–Ni–S2	78.92(5)	Ni–P2–C22	120.5(2)
P2–Ni–S2	96.55(6)	Ni–P2–C21	111.1(2)
P2–Ni–S1	172.99(5)	C22–P2–C23	106.0(2)
P1–Ni–S2	175.24(6)	C21–P2–C23	105.9(3)
P1–Ni–S1	96.82(5)	C21–P2–C22	103.2(2)
P1–Ni–P2	87.48(5)	Ni–S1–C1	86.2(2)
Ni–P1–C13	109.9(2)	Ni–S2–C1	86.3(2)
Ni–P1–C12	117.0(2)	S2–C1–S3	125.9(3)
Ni–P1–C11	114.1(2)	S1–C1–S3	125.8(3)
C12–P1–C13	104.3(3)	S1–C1–S2	108.2(3)
C11–P1–C13	107.5(3)	P2–C23–C13	107.9(4)
C11–P1–C12	103.2(2)	P1–C13–C23	109.1(4)
Ni–P2–C23	109.1(2)		

moiety, which is also manifested in the short Ni—C1 and Ni—S1 contacts of 1.94(1) and 2.130(3) Å, respectively.

The geometry around the Ni center in the 1,1′-dithiolate complex 4 is distorted square planar, the two PMe_2 groups being essentially trans with respect to the sulfur atoms. Some deviation toward tetrahedral geometry is apparent. The P1–Ni–S1 and P2–Ni–S2 angles are 173.37(6) and 175.23(7)°, respectively, with P1 and S1 deviating by 0.1 and 0.07 Å from the best mean-square coordination plane and P2 and S2 exhibiting similar departures of 0.06 Å, although in the opposite direction. The major distortion, however, is introduced by the S_2CRR' ligand that has a bite angle of only 80.12(6)°, a value nevertheless larger than those found in related complexes, e.g., 73.58° in the mononuclear $Cp^*Rh(S_2CH_2)(PMe_3)$[1g] and 72.45(4)° in the binuclear iron derivative $Fe_2(S_2CH_2)(CO)_6$.[16a] The strain of the four-membered NiS_2C ring is evidenced by the appreciable deviation of the S1–C1–S2 angle (98.8(2)°) with respect to the ideal tetrahedral value. While this deviation is very small in the above Rh complex (104.8°), related binuclear complexes containing μ-S_2CH_2 entities are characterized by S–C–S angles[16a,e] of about 94°. Other structural features of the molecules of 4 are normal, for instance, the C1–S bond lengths (1.84 Å av) are typical of C–S single bonds, and the Ni–S and Ni–P separations are similar to those found in other related complexes.[6,17d]

The trithiocarbonate complex 5 also exhibits a distorted square-planar geometry around the nickel center. The trithiocarbonate ligand is essentially planar (the C1 atom deviates slightly (0.012(4) Å) from planarity) and bonds to the metal atom through two of its sulfur atoms, forming a four-membered NiS_2C ring similar to that found[33] in $Ni(CS_3)_2^{2-}$ and related complexes.[17] The small bite angle of the CS_3^{2-} ligand in 5 (78.92(5)°) is somewhat larger that those found in the above-mentioned Ni complex and in the Co derivative[34] $CpCo(CS_3)(CNBu^t)$ (ca. 76–77°). In correspondence with other M–CS_3 complexes,[17,33,34] a considerable distortion of the S–C–S angles from the ideal 120° value corresponding to trithiocarbonic acid is found in 5. Thus, the exocyclic S1–C1–S3 and S2–C1–S3 angles have magnitudes close to 126° (see Table 3), while the endocyclic S1–C1–S2 angle is significantly smaller (108.2(3)°). The three C–S bonds are relatively short, indicating some multiple bond character which, as expected, is significantly larger for the C–S bond to the uncoordinated sulfur (C1–S3 = 1.648(5) vs 1.723(5) Å av for the other two C–S bonds). Other bonding parameters are normal and require no comment.

Discussion

Although complex 1a has already been fully characterized,[6a] it is worth recalling here, with due brevity, some important properties relevant to the results described in the previous sections and the discussion that follows. Compound 1a is a highly fluxional molecule in solution: the two PMe_3 groups undergoing fast intermolecular exchange at room temperature even with trace amounts of the free ligand.[35] Due to the higher trans effect of the Ni–alkyl bond, as compared to the Ni–aryl, this exchange is faster for the *trans*-CH_2-NiPMe_3 phosphine. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ low-temperature NMR studies indicate that the concentration of the putative 5-coordinated tris(phosphine) intermediate remains low at −80 °C, even in the presence of 4 equiv of added PMe_3. These observations clearly indicate that (i) there is a coordination site already available, at least for small molecules, and (ii) the *trans*-CH_2-Ni-PMe_3 phosphine is more labile than the other.

It is appropriate, both conceptually and didactically, to start this section with a discussion of the reactions of 1a with CO and $CNBu^t$. The insertion of CO into the Ni–C

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[33] McKechnie, J. S.; Miesel, S. L.; Paul, I. C. *J. Chem. Soc., Chem. Commun.* 1967, 152.

[34] Doherty, I.; Fortune, J.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1984, 1111.

[35] Further NMR observations in accord with the intermolecular nature of this exchange are provided in the following: Belderraín, T. R.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Paneque, M.; Poveda, M. L. *Organometallics* 1993, *12*, 4431.

Table 4. Crystal and Refinement Data for 3a, 4, and 5

	3a	**4**	**5**
formula	$C_{17}H_{30}NiP_2S_2{\cdot}{}^1/_2C_4H_{10}O$	$C_{17}H_{28}NiP_2S_2$	$C_7H_{16}NiP_2S_3$
mol wt	464.5	417.2	316.7
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$
cell dimens			
a, Å	19.847(8)	11.888(4)	14.286(5)
b, Å	9.343(2)	14.073(3)	7.486(1)
c, Å	13.939(3)	25.065(3)	12.692(1)
β, deg	109.79(3)		93.40(2)
Z	4	8	4
V, Å^3	2432(1)	4193(1)	1355.0(5)
D_{calcd}, g cm^{-3}	1.271	1.322	1.554
F(000)	972	1760	656
temp, K	295	295	295
diffractometer	Enraf-Nonius	Enraf-Nonius	Enraf-Nonius
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	graphite-monochromated Mo Kα (λ = 0.710 69 Å)	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
μ(Mo Kα), cm^{-1}	11.01	12.66	20.77
crystal dimens, mm	0.3 × 0.4 × 0.5	0.2 × 0.4 × 0.5	0.2 × 0.3 × 0.5
2θ range, deg	1–50	1–56	1–50
scan technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
data collected	(–23,0,0) to (23,11,16)	(0,0,0) to (15,18,33)	(0,0,–17) to (20,10,17)
no. of unique data	4258	5155	3931
no. of obsd reflctns	2765	2473	2358
decay	30%		
no. of standard reflctns	3	3	3
weighting scheme	unit	unit	unit
$R = \sum\|\Delta^2F\|/\sum\|F_o\|$	7.1	3.5	3.5
$R_w = (\sum w\Delta^2F/\sum w\|F_o\|^2)^{1/2}$	7.8	3.5	3.9
maximum shift/error	0.05	0.028	0.023

bonds of **1a** can be suggested to occur through a 5-coordinate intermediate related to **I** which then evolves to the insertion products,[36] as shown in eq 10. The proposed regiochemistry (namely insertion into the Ni–alkyl bond) can be accounted for considering the greater migratory capability of the alkyl chain as compared to the Ni–aryl bond.[37] The experiment depicted in eq 14 suggests, in

$$[Ni]\text{–}C(O)Ph + [Ni]\text{–}Me \rightleftharpoons [Ni]\text{–}Ph + [Ni]\text{–}C(O)Me \quad (14)$$

$$[Ni] = trans\text{-}Ni(Br)(PMe_3)_2$$

addition, that intermediate **H** (eq 10) is also the thermodynamic product of this transformation. Interestingly, while **H** readily undergoes CS_2 insertion into the Ni–aryl bond (Scheme 4), no additional reaction with excess CO is observed, and only the reductive elimination products are obtained. This is in line with the analogous incorporation of CO into other metallacycles[4c,24,37–39] which undergo only monoinsertion of CO and also with the high tendency of Ni(C(O)R)R′ species to reductively eliminate the corresponding ketone, RC(O)R′, particularly in the presence of CO.[40] The existence of the chelating ligands in metallacycles **1b** and **1c** makes these compounds much less susceptible to CO insertion. Again, this is in common with the behavior found for other related species. Usually, nickelacycles containing chelating ligands are unreactive toward CO unless these ligands are sufficiently electron releasing.[24,39,41] In the case of, for example, $Ni(CH_2CH_2CH_2CH_2)(Ph_2PCH_2CH_2PPh_2)$,[24] it has been argued that the reduced reactivity is due to the incapability of the complex to form the 5-coordinate carbonyl intermediate. More recently these arguments have been put forward in terms of the concept of geometrical rigidity, defined[42] as the reluctance of a complex that contains rather rigid ligands to undergo changes in the bonding angles.

With regard to the reaction of **1a** with $CNBu^t$, an adduct **1a·CNBu^t** analogous to **I** can be proposed to form, but this does not evolve to the isocyanide insertion product. Instead, PMe_3 substitution is more favorable, and the resulting species **10** is stable toward insertion. This behavior resembles that found in some platinacycles[38f] but contrasts with the facility with which other Ni–alkyl and Ni–aryl complexes undergo CNR insertion.[27b,43,44]

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[36] This reaction scheme for the formation of NiC(O)R species is frequently invoked in the literature. For some of the most interesting earlier studies, see: (a) Stoppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 718. (b) Maruyama, K.; Ito, T.; Yamamoto, A. *J. Organomet. Chem.* **1978**, *157*, 463.

[37] Related zirconacycles exhibit the same selectivity: (a) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45. (b) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

[38] See for example: (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (b) Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1978**, *161*, 371. (c) Foulger, B. E.; Grevels, F.-W.; Hess, D.; Kroerner, v. Gustorf, E. A.; Leitich, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1451. (d) Diversi, P.; Ingrosso, G.; Lucherini, A.; Murtas, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1633. (e) Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318. (f) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147.

[39] (a) Jolly, P. W.; Krüger, C.; Salz, R.; Sakutowski, J. C. *J. Organomet. Chem.* **1979**, *165*, C39. (b) Eisch, J. J.; Pietrowski, A. M.; Aradi, A. A.; Krüger, C.; Romão, M. J. *Z. Naturforsch.* **1985**, *40b*, 624. (c) Pasto, D. J.; Huang, N.-Z. *Organometallics* **1985**, *4*, 1386. (d) Eisch, J. J.; Pietrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y.-H. *Organometallics* **1985**, *4*, 224. (e) Mynott, R.; Neidlein, R.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 640.

[40] Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2161.

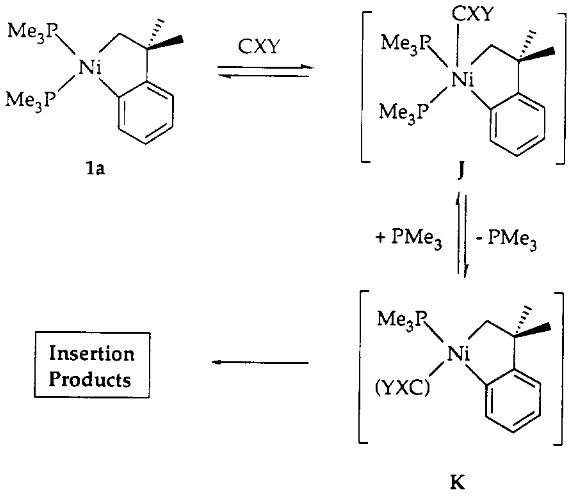
[41] Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376.

[42] Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 3806.

[43] (a) Bochmann, M.; Hawkins, I.; Sloan, M. P. *J. Organomet. Chem.* **1987**, *332*, 371. (b) Carmona, E.; Marín, J. M.; Palma, P.; Poveda, M. L. *J. Organomet. Chem.* **1989**, *377*, 157. (c) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Ruíz, C.; Carmona, E. *Organometallics* **1993**, *12*, 4025.

[44] Unpublished observations from this laboratory indicate that *trans*-$NiBr(PMe_3)_2Ph$ readily inserts $CNBu^t$ to give *trans*-$NiBr(PMe_3)_2(\eta^1\text{-}C({=}NBu^t)Ph)$. See also: Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101.

Scheme 7



Complex **1a** reacts with various heterocumulenes, X=C=Y. The insertion of CO_2 to give the nickelalactone species $(Me_3P)_2\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(=O)O})$ has already been described;[6a] the reactions with CS_2, COS, PhNCS, PhNCO and $C(NC_6H_4\text{-}p\text{-}Me)_2$ are the aim of this contribution. The reactivity order found is $CS_2 \sim COS \sim PhNCS > PhNCO > C(NC_6H_4\text{-}p\text{-}Me)_2 \gg CO_2$. Thus, the three S-containing molecules react instantaneously[45] at temperatures as low as -80 °C, while with PhNCO and $C(NC_6H_4\text{-}p\text{-}Me)_2$, product formation starts at -60 °C, and CO_2 requires days at room temperature.

An interesting feature of the above findings is the very high reactivity toward CS_2 exhibited by **1a**, which markedly contrasts with the slowness of the analogous CO_2 reaction. CS_2 insertion into M–C bonds is not, generally, a very favorable process.[13,46] For example, R–M(CO)$_5$ derivatives (M = Mn, Re) require[47] high temperatures and pressures in neat CS_2, and for the formation of *trans*-$Pd(\eta^2\text{-}S_2CCH_3)I(PMe_3)_2$ from *trans*-$Pd(CH_3)I(PMe_3)_2$ and neat CS_2, 48 h at 20 °C is needed.[48] No insertion is observed for the cationic species[48] $[Pd(CH_3)(PMe_3)_3]^+$ or for the neutral phenyl complex *trans*-$Ni(C_6H_5)Br(PMe_3)_2$.[49] Literature reports on relative rates of CO_2 and CS_2 insertions into M–C bonds are very scarce, but CS_2 incorporation seems somewhat more favorable.[12e,50]

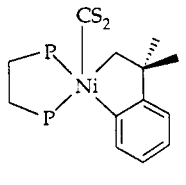
A tentative mechanism for heterocumulene reactivity toward **1a** is presented in Scheme 7. This is based on that proposed by Bergman for alkyne insertion into $Ni(CH_3)(acac)(PPh_3)$[51] and postulates a preequilibrium step involving adduct **K**. In accord with this mechanism, a strong inhibiting effect is evidenced when the reaction of **1a** and PhNCO is carried out in the presence of added PMe_3.[52] In adduct **K**, the cumulene could adopt an η^1 or an η^2 bonding mode,[3] with the softer atom of the nonsymmetric heterocumulene directly bonded to the Ni center (i.e., with a preference order S > N > O). Once this adduct is formed, CXY insertion into the Ni-aryl bond would give the corresponding heterometallacycles.

Interestingly, the kinetic insertion product of CS_2 and **1a**, **A**, contains the resulting dithiocarboxylate group η^3-*S,C,S'*-bonded to the metal, as revealed by low-temperature NMR studies. Although dithiocarboxylate complexes of Ni(II) are known in different coordination modes,[3b] the trihapto Ni-S_2C-linkage found for intermediate **A** has not been observed previously. The 7-membered heterometallacycles resulting from the insertion of other heterocumulenes are 16-electron species, but some of these compounds have been shown to react with PMe_3 to afford the corresponding closed-shell tris(phosphine) adducts. As shown in Scheme 2, the η^3-*S,C,S'*-bonding in **A** can be disrupted by addition of PMe_3 or dmpe.

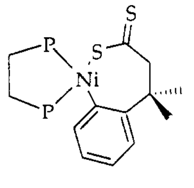
Finally, in this regard, the very low reactivity of **1a** against CO_2 may be due to the low affinity of the Ni(II) center for the C=O double bonds, which we believe it is also responsible for the regioselectivity observed in the PhNCO reaction.

The heterometallacycles resulting from the incorporation of the cumulene into the Ni–aryl bond are of variable stability. Those derived from CS_2, COS, and PhNCS are unstable and undergo reductive elimination with concomitant C–S bond formation. For CS_2, this product is the dithiolactone **2**, which remains coordinated to the metal, forming complex **3a**, a novel example of an organometallic derivative of an η^2-C=S ligand. Compounds of this type are of relevance for the desulfurization reaction.[30,53]

The reaction of **1b** with dmpe gives the 1,1-dithiolate complex **4** (eq 5), which in a formal sense can be considered as the product of the insertion of CS_2 into the two Ni–C bonds of the nickelacycle. Although other *gem*-dithiolates are known,[1a,g,16] in no case, however, has this kind of functionality be generated using CS_2 as a reagent. In light of the above results, and taking into account the feasibility of adducts of type **I**, it seems reasonable to propose that this reaction proceeds through the intermediacy of a CS_2 adduct of type **L**. The trans labilizing effect of the Ni–



L



M

CH_2 moiety is rendered inoperative by the chelating diphosphine. CS_2 insertion could occur either in the Ni–aryl or in the Ni–alkyl bond. In the first case, intermediate **C** would be generated, which indeed forms **4** at higher temperatures, but, as already mentioned, competition experiments clearly show that **C** is not an intermediate in the reaction pathway from **1b** to **4**. Hence we are left with the possibility of CS_2 inserting into the more labile Ni–alkyl bond to afford an alkyl dithiocarboxylate functionality of the type depicted in **M**. Intramolecular C–C coupling followed by coordination of the exocyclic sulfur

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(45) A competition experiment carried out with **1a** and equivalent amounts of CS_2 and SCNPh at -80 °C reveals that CS_2 reacts about twice as fast as PhNCS. This result indicates that the C=S functionalities of both reagents have approximately the same reactivity toward insertion.

(46) (a) Camus, A.; Marsich, N.; Nardin, G. *J. Organomet. Chem.* **1980**, *188*, 389. (b) Otto, H.; Werner, H. *Chem. Ber.* **1987**, *120*, 97. (c) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223.

(47) Lindner, E.; Grimmer, R.; Weber, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 639.

(48) Werner, H.; Bertleff, W. *Chem. Ber.* **1980**, *113*, 267.

(49) Palma, P., unpublished observations.

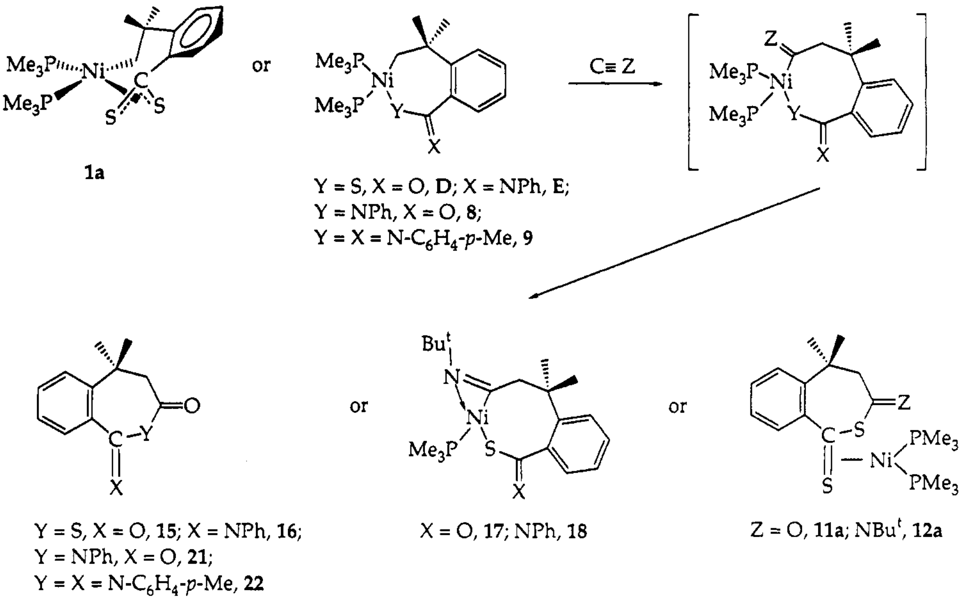
(50) Darensbourg, D. J.; Wiegreffe, H. P.; Reibenspies, J. H. *Organometallics* **1991**, *10*, 6.

(51) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

(52) Probably due to the very fast reaction with CS_2, no such qualitative inhibition effect by PMe_3 can be noticed at -80 °C.

(53) Eisch, J. J.; Hallenbeck, L.; Han, K. I. *J. Am. Chem. Soc.* **1986**, *108*, 7763 and references therein.

Scheme 8



1a

Y = S, X = O, **D**; X = NPh, **E**;
Y = NPh, X = O, **8**;
Y = X = N-C_6H_4-*p*-Me, **9**

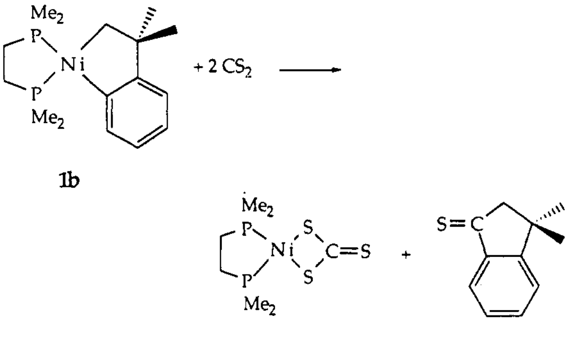
Y = S, X = O, **15**; X = NPh, **16**;
Y = NPh, X = O, **21**;
Y = X = N-C_6H_4-*p*-Me, **22**

X = O, **17**; NPh, **18**

Z = O, **11a**; NBu^t, **12a**

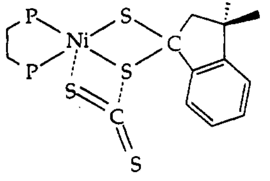
would afford the final observed product. The influence of the phosphine groups in this intraligand coupling reaction (C–S for PMe_3, C–C for dmpe) is not presently understood.

The 1,1-dithiolate **4** and CS_2 react further, forming the trithiocarbonate **5** and the thioketone **6**. The overall reaction, starting from **1b** and CS_2, can be represented as shown in eq 15 and corresponds, formally, to a reductive disproportionation[3] of CS_2 (i.e., $2CS_2 + 2e \rightarrow CS_3^{2-} + CS$) induced by the Ni center. Curiously, the thiocarbonyl unit resulting from this reaction becomes incorporated into the thioketone functionality. Equation 15 is highly reminiscent of the analogous reaction of **1a** with CO_2 to give a Ni–CO_3^{2-} complex and the corresponding ketone.[6a] Interestingly, the above reaction takes place without change in the oxidation state of the nickel center. Hence, the required two electrons are provided, once again in a formal sense, by the organic fragment.



1b **5** **6** (15)

Mechanistically, the reaction of **4** with CS_2 may involve a CS_2-induced reductive elimination with S–S bond formation, yielding an unstable dithiirane[54] which would quickly transfer one of its sulfur atoms to yield the observed products. A direct attack of the entering CS_2 molecule on one of the Ni–S bonds of **4** (**N**), in a process resembling some heterocumulene exchange reactions,[17a] seems, however, more likely.



N

The heterometallacycles resulting from the insertion of the heterocumulenes, CXY, into the Ni–aryl bond of **1a** contain seven-membered rings that incorporate one sulfur or nitrogen atom in addition to the Ni atom. Metallacycles of this type are usually susceptible to ring-contraction in a process that involves β-H elimination.[23b,55] The lack of β-Hs in these complexes avoids this undesired transformation and allows one to take advantage of the presence in their molecules of a reactive Ni–CH_2 bond, susceptible to undergo further insertion chemistry. It should be noted that, probably due to subtle mechanistic factors, while **1a** does not undergo CNBu^t insertion, the metallacycles derived from the incorporation of CXY into the Ni–aryl bond react cleanly and quickly with this molecule. As expected, they also interact rapidly with CO.

Three types of compounds can be isolated depending upon the nature of the starting heterometallacycle and incoming reagent (Scheme 8). Thus, the successive insertions of CS_2 and CO or CNBu^t give rise to organometallic compounds of Ni(0) (**11a** and **12a**, respectively) that contain a Ni—η^2-C=S moiety. If a >C=S bond is not available in the starting metallacycle, the reaction product depends upon the nature of the incoming molecule, CNBu^t or CO. Thus, the former affords stable η^2-iminoacyls (**17** and **18**), while for CO the corresponding acyls are unstable and undergo reductive elimination with evolution of the free organic molecules (e.g., **15** and **16**).

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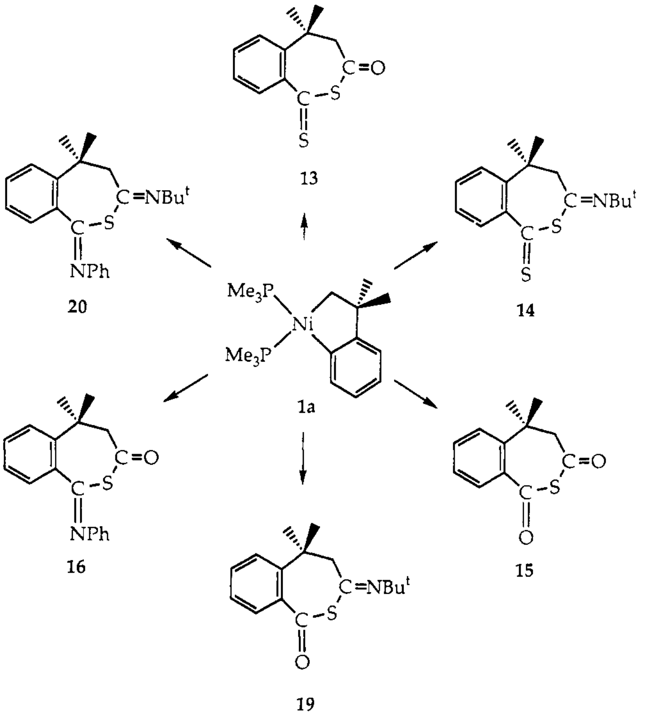
(54) Dithiiranes are very unstable, nonisolable molecules. See: (a) Zoller, U. In *Heterocyclic Compounds*; Hassner, A. Ed., Wiley: London, 1983; Vol. 42, p 608. (b) Snyder, J. P.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, *99*, 2931. Very recently a derivative of such a ring has been isolated: Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Nakayama, J.; Hoshino, M. *J. Am. Chem. Soc.* **1993**, *115*, 4914.

(55) Yamamoto, T.; Sano, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1987**, *109*, 1092.

Scheme 9



Scheme 9 summarizes the organic products resulting from the sequential sulfur-containing heterocumulene–CO or -CNBu^t incorporations into the Ni–C bonds of **1a**. These products are obtained either directly, from the above consecutive reactions, or by the methods described in the Results section. As can be seen, this methodology has been applied to the synthesis of thione analogs of acid anhydrides and to that of related imine derivatives. The thione analogs of acid anhydrides are compounds of considerable interest, and although some stable derivatives have been prepared recently, they are generally rather unstable and elusive molecules.[25] As already mentioned, the synthetic approach that successfully allows the formation of these substances relies on the regioselective insertion of the heterocumulene into the Ni–aryl bond of **1a**, to yield reactive 7-membered heterometalacyclic species able to undergo additional insertion of CO or CNBu^t into the Ni–alkyl bond.

Conclusions

The work described in this contribution demonstrates that the Ni–aryl bond of the nickelacycle $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1a**) is very prone to undergo insertion of a variety of heterocumulenes, X=C=Y, with formation of seven-membered heterometallacycles of disparate thermal stability. This transformation activates the preexisting Ni–CH$_2$ bond toward the insertion of CO or CNBu^t, allowing the synthesis, either directly or by further elaboration of the primary product of the insertion reaction, of a variety of seven-membered organic heterocycles. Contrary to the reaction of **1a** with CS$_2$, the related metallacycle $(dmpe)Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1b**), which contains a chelating phosphine ligand, experiences, under analogous conditions, an unprecedented transformation that yields the 1,1-dithiolate complex **4**, formally the product of the insertion of CS$_2$ into the two Ni–C bonds of **1b**.

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Remagen, Germany, and the Analytical Service of the University of Sevilla. The spectroscopic instruments used were Perkin-Elmer Models 577 and 684 for IR spectra, Varian XL-200 for NMR, and Kratos MS-80 for mass spectroscopy. The ^{13}C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to SiMe$_4$. The ^{13}C{^{1}H} NMR assignments were helped in most cases with the use of gate decoupling and APT techniques. ^{31}P{^{1}H} NMR shifts are referenced to external 85% H$_3$PO$_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. The compounds **1a**,[6a] **1b**,[6b] PMe$_3$,[56] and CNBu^t[57] were prepared according to literature methods.

Synthesis of (bipy)Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$) (1c). To a solution of **1a** (0.34 g, 1 mmol) in Et$_2$O (30 mL) was added 0.1 g of solid bipy (1 mmol). The resulting dark green mixture was stirred at room temperature for 20 min and then taken to dryness. Extraction with Et$_2$O, filtration, and cooling at -15 °C furnished very dark green crystals of complex **1c**: combined yield of two crops, 70%; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, 20 °C) δ 1.43 (s, 6 H, CMe$_2$), 1.94 (s, 2 H, CH$_2$), 5.3–9.1 (m, aromatics); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ 33.9 (C*Me*$_2$), 44.3 (CH$_2$), 47.9 (*C*Me$_2$), 120.5, 121.0, 122.8, 123.5, 126.0, 126.3, 136.1, 137.6, 148.9, 151.1 (1:2:1:1:1:1:2:1:1:1 relative ratio, aromatic C–H carbons), 154.1, 154.9, 163.0, 170.8 (aromatic quaternary carbons). Anal. Calcd for C$_{20}$H$_{20}$N$_2$Ni: C, 69.9; H, 5.8. Found: C, 69.1; H, 5.9.

Reaction of 1a with Excess of CS$_2$. To a cold (-50 °C), stirred solution of **1a** (0.34 g, 1 mmol) in Et$_2$O (30 mL) was added 4 equiv of CS$_2$ (4 mL of a 1 M solution in toluene) *via* syringe. The cooling bath was removed, and upon warming the dark solution developed a red-orange coloration. After the solution was stirred for 2 h at room temperature, a brown microcrystalline precipitate, identified as Ibers's complex,[10] was filtered and washed with Et$_2$O. The red filtrate was evaporated to dryness and the residue extracted with 20 mL of petroleum ether. The last operation was repeated, and after concentration of the extract and cooling at -30 °C, compound **2** was obtained in the form of dark red needles: yield, 80%; ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C) δ 1.03 (s, 6 H, CMe$_2$), 2.30 (s, 2 H, CH$_2$), 6.9–8.5 (m, aromatics); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 27.4 (C*Me*$_2$), 34.2 (*C*Me$_2$), 42.4 (CH$_2$), 124.2, 126.6, 129.4, 133.4 (aromatic C–H carbons), 137.8, 143.0 (aromatic quaternary carbons), 224.7 (C=S); IR (Nujol mull) ν(C=S) 1020 s. Anal. Calcd for C$_{11}$H$_{12}$S$_2$: C, 63.4; H, 5.8. Found: C, 63.4; H, 6.0.

The ^{13}CS$_2$-enriched dithiolactone **2*** was obtained by the following procedure: 1 equiv of 50%, ^{13}C-enriched CS$_2$ was added at -50 °C to a solution of **1a**. The cooling bath was then removed, and after the solution was stirred for 10 min, 3 equiv more of CS$_2$, this time of normal isotopic composition, was introduced into the flask. Workup as above furnished ^{13}C-labeled **2***. Selected data for **2***: ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ 137.7 (d, C_{ar}-*C(=S), $^1J_{CC}$ = 50 Hz); IR (Nujol mull) ν(^{13}C=S) 1000 s.

Synthesis of (Me$_3$P)$_2$Ni(η^2-S=CSCH$_2$CMe$_2$-*o*-C$_6$H$_4$) (3a). CS$_2$ (1 mmol, 1 mL of a 1 M solution in toluene) was added to a cold (-90 °C) solution of **1a** (0.34 g, 1 mmol) in Et$_2$O (40 mL); the original orange color of **1a** suddenly changed to the very dark green, almost black, characteristic coloration of intermediate **A**. Upon gentle warming of the solution to -60 °C, a further change was observed to a reddish orange color. The solvent was removed under vacuum while the temperature was kept at 0 °C, and the resulting orange microcrystalline residue was washed with 20 mL of petroleum ether: yield of crude product, 80%. Complex

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(56) (a) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149. (b) Luetkens, M. L., Jr.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P., Jr. *Inorg. Synth.* **1990**, *28*, 305.

(57) Gokel, G. W.; Widera, R. P.; Weber, W. P. *Org. Synth.* **1976**, *55*, 96.

3a can be crystallized from Et_2O as well-formed red prisms of composition $\mathbf{3a}\cdot 0.5\,Et_2O$. ***Note***: It is very important to evaporate the volatiles at 0 °C, otherwise decomposition to insoluble tars readily occurs. Once isolated, complex **3a** is a very stable compound, even in solution, and therefore its decomposition when in the crude mixture may be due to the catalytic action of unknown impurities: ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 0.90 (br s, 18 H, PMe_3), 1.20, 1.48 (s, 3 H and 3 H, CMe_2), 2.46, 3.31 (d, $^2J_{HH}$ = 13 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 7.0–8.2 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) AX spin system, $\delta_A = -8.4$, $\delta_X = -7.0$, $^2J_{AX} = 7$ Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 16.3 (d, $^1J_{CP}$ = 24 Hz, PMe_3), 18.0 (d, $^1J_{CP}$ = 23 Hz, PMe_3), 30.8 (s, $C\mathit{Me}_2$), 35.3 (s, $\mathit{C}Me_2$), 45.8 (s, CH_2), 68.5 (br s, C=S), 123.8, 124.5, 126.6, 130.7 (s, aromatic C–H carbons), 143.9, 149.5 (s, aromatic quaternary carbons). The signal due to the C=S carbon appears as a doublet at low temperature: δ 58.0, $^2J_{CP}$ = 34 Hz; M_w (cryoscopically, C_6H_6, N_2) calcd for $C_{17}H_{30}P_2S_2Ni$ 419, found 416. Anal. Calcd for $C_{17}H_{30}P_2S_2Ni\cdot{}^1/_2\,(C_2H_5)_2O$: C, 49.9; H, 7.6. Found: C, 49.4; H, 7.2.

By carrying out the reaction with ^{13}C-enriched CS_2, complex **3a*** was similarly prepared. The $^{31}P\{^1H\}$ NMR spectrum of **3a*** (CD_2Cl_2, −70 °C) shows that the phosphorus resonance that appears at −8.4 ppm in the spectrum of **3a** is further split by coupling to ^{13}C ($^2J_{PC}$ = 33 Hz).

Spectroscopic data for the green intermediate $(Me_3P)_2Ni(\eta^3\text{-}S_2CC_6H_4\text{-}o\text{-}CMe_2CH_2)$ (**A**): $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 17.0 (d, $^1J_{CP}$ = 19 Hz, PMe_3), 35.4, 38.5 (br s, $C\mathit{Me}_2$), 36.8 (d, $^2J_{CP}$ = 23 Hz, CH_2), 39.4 (d, $^3J_{CP}$ = 6 Hz, $\mathit{C}Me_2$), 124.5, 127.0, 127.7 (aromatic C–H carbons), 131.7 (d, J_{CP} = 8 Hz, aromatic C–H carbon), 145.5, 149.5 (d and t, J_{CP} = 7 and 5 Hz, respectively, aromatic quaternary carbons); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) AX spin system, $\delta_A = -19.0$, $\delta_X = 9.6$, $^2J_{AX} = 8$ Hz. For **A*** ($^{13}CS_2$-enriched sample), the first resonance is coupled to the ^{13}C nuclei ($^2J_{PC}$ = 18 Hz): $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 137.1 (d, $^2J_{CP}$ = 19 Hz, CS_2), 145.5 (dd, $^1J_{CC}$ = 55 Hz, J_{CP} = 7 Hz, aromatic quaternary carbon).

As described in the Results, the dark green intermediate **A** reacts reversibly, at −80 °C, with an excess of PMe_3 to give the brown tris(phosphine) species $(Me_3P)_3Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C({=}S)S)$ (**B**), fully characterized by the following spectroscopic data: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) AMX spin system, $\delta_A = -34.9$, $\delta_M = -12.9$, $\delta_X = -5.3$, $^2J_{AM} = 182$, $^2J_{MX} = 43$ Hz, $^{13}C\{^1H\}$ NMR (CD_2Cl_2–Et_2O, −90 °C, $^{13}CS_2$-enriched sample) δ 124.7, 126.6, 128.4 (s, 2:1:1 ratio, aromatic C–H carbons), 145.5 (s, aromatic quaternary carbon), 258.0 (S_2CR) (the C_{ar}-$^*CS_2$ could not be positively identified). This complex decomposes in the presence of PMe_3 at −60 °C with formation of **3a**.

Synthesis of (dmpe)Ni(η^2-S=CSCH$_2$CMe$_2$-*o*-C$_6$H$_4$) (3b). Complex **3a** (0.42 g, 1 mmol) was dissolved in Et_2O (20 mL) at room temperature, and to this solution was added 1 equiv of dmpe (0.15 mL, 1 mmol) without stirring, in such a way that this reagent reached the main solution slowly down the walls of the flask. The mixture was left undisturbed for 2 h, and the resulting dark red crystals were decanted off, washed with petroleum ether, and dried under vacuum: yield, 87%; ^1H NMR (200 MHz, CD_2Cl_2, 20 °C) δ 1.37 (filled in doublet, $J_{HP_{app}}$ = 10 Hz, 6 H, 2 P-Me), 1.32 (br s, 6 H, CMe_2), 1.66 (pseudotriplet, $J_{HP_{app}}$ = 2.1 Hz, 6 H, 2 P-Me), 2.05 (m, 4 H, 2 P-CH_2), 2.55, 2.80 (d, $^2J_{HH}$ = 13.1 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.7–7.5 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 46.4; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 13.8, 14.8 (m, P-Me), 28.5 (t, $J_{CP_{app}}$ = 23 Hz, P-CH_2), 29.6 (t, $J_{CP_{app}}$ = 14 Hz, P-CH_2), 30.8, 31.0 ($C\mathit{Me}_2$), 35.3 (s, $\mathit{C}Me_2$), 44.3 (s, S-CH_2), 64.0 (br s, C=S), 123.9, 126.4, 130.1 (s, 2:1:1 ratio, aromatic C–H carbons), 142.8, 148.5 (s, aromatic quaternary carbons). Anal. Calcd for $C_{17}H_{28}P_2S_2Ni$: C, 48.9, H, 6.8. Found: C, 48.7; H, 7.4.

Reaction of 3a with CO. Carbon monoxide was bubbled, at room temperature and pressure, through a solution of **3a** (0.21 g, 0.5 mmol) in CH_2Cl_2 (10 mL) for ca. 5 min. During this process, the color changed from orange to red-violet. The solution was stripped to dryness and the resulting residue extracted with 10 mL of petroleum ether. Filtration, concentration, and cooling at −30 °C furnished the crystalline dithiolactone **2** in 75% yield.

Synthesis of (dmpe)Ni(η^2-S$_2$CCH$_2$CMe$_2$-*o*-C$_6$H$_4$) (4). To a solution of complex **1b** (0.34 g, 1 mmol) in acetone (20 mL) was added 1 mL of a 1 M solution of CS_2 in toluene *via* syringe. After being stirred for a few minutes at room temperature, the resulting solution was filtered, concentrated, and cooled at −30 °C. Complex **4** was obtained as an orange crystalline material in 75% yield: ^1H NMR (200 MHz, CD_2Cl_2, 20 °C) δ 1.33 (s, 6 H, CMe_2), 1.38 (pseudotriplet, $J_{HP_{app}}$ = 5.5 Hz, 6 H, 2 P-Me), 1.40 (pseudotriplet, $J_{HP_{app}}$ = 5.5 Hz, 6 H, 2P-Me), 2.50 (s, 2 H, CH_2), 7.0–7.7 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 42.9; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 12.5 (m, P-Me), 27.4 (t, $J_{CP_{app}}$ = 24 Hz, P-CH_2), 30.6 (s, $C\mathit{Me}_2$), 42.8 (s, $\mathit{C}Me_2$), 66.2 (s, CS_2), 67.0 (s, S_2CCH_2), 121.4, 124.8, 126.6 (s, 1:1:2 ratio, aromatic C–H carbons), 148.8, 153.3 (s, aromatic quaternary carbons). Anal. Calcd for $C_{17}H_{28}P_2S_2Ni$: C, 48.9; H. 6.8. Found: C, 48.9, H, 6.9.

By using ^{13}C-enriched CS_2, a sample of ^{13}C-labeled **4*** was obtained: ^1H NMR (CD_2Cl_2, 20 °C) δ 2.50 (d, $^2J_{HC}$ = 4.5 Hz, CH_2); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 20 °C) δ 67.7 (d, $^1J_{CC}$ = 36 Hz, $S_2{}^*C\mathit{C}H_2$), 154.7 (d, $^1J_{CC}$ = 45 Hz, $S_2{}^*CC_q$).

Reaction of A with dmpe. Observation of (dmpe)Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$C(=S)S (C). Complex **A** (0.5 mmol) was prepared *in situ* at −90 °C by carefully mixing cooled CH_2Cl_2 solutions of CS_2 and **1a** (1:1 ratio). The resulting dark green solution was immediately treated with 0.5 mL of a cold 1 M dmpe solution in CH_2Cl_2. A fast reaction was noticed as the color of the solution suddenly changed to the characteristic orange of **C**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) AX spin system, $\delta_A = 30.1$, $\delta_X = 45.7$, $^2J_{AX}$ = 27 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 10–20 (m, P-Me, obscured by free PMe_3), 25–27 (complex multiplets, Ni-CH_2 and P-CH_2), 33.5, 34.8 (s, $C\mathit{Me}_2$), 39.7 (s, $\mathit{C}Me_2$), 123.1, 124.7, 127.6 (s, 1:2:1 ratio, aromatic C–H carbons), 144.2, 153.3 (s, aromatic quaternary carbons).

A $^{13}CS_2$-enriched sample of **C** showed the following characteristics: $^{13}C\{^1H\}$ NMR δ 153.3 (d, $^1J_{CC}$ = 49 Hz, C_{ar}-$^*C({=}S)$), 256.0 (s, C=S).

Complex **C** decomposed cleanly in CH_2Cl_2 at temperatures above −50 °C with formation of **4** in a reaction that constitutes an alternative method for the synthesis of the *gem*-dithiolate **4**. To a solution of complex **1a** (0.34 g, 1 mmol) in 20 mL of cold (−80 °C) Et_2O was added with stirring 1 equiv of CS_2 (1 mL of a 1 M solution in toluene). The dark green mixture was stirred at that temperature for 2–3 min, and then 10 mL of a cold (−80 °C) 0.1 M Et_2O solution of dmpe was slowly introduced into the reaction flask. An intermediate reaction took place with formation of a dark red precipitate. The cooling bath was then removed, and at ~0 °C, the color of the precipitate material changed to yellow-orange. This solid was filtered, washed with Et_2O, and dried *in vacuo* to give complex **4** as a yellow-orange microcrystalline material: yield, 75%.

Reaction of the *gem*-Dithiolate 4 with Excess CS$_2$. To a solution of complex **4** (0.42 g, 1 mmol) in acetone (15 mL) was added 2 mL of a 1 M solution of CS_2 in toluene. After being stirred at room temperature for 7 h, the reaction mixture was filtered to furnish complex **5** as a yellow microcrystalline solid. The filtrate was taken to dryness and the residue extracted with petroleum ether, leaving behind additional amounts of **5**. The last operation was repeated twice to give further crops of this complex (combined yield, 95%) and a violet solution of the thioketone **6** (0.04 g, 80% yield). Compound **5** can be purified by crystallization from hot dimethyl sulfoxide, while the liquid violet thioketone **6** can be distilled under reduced pressure.

Complex **5**: ^1H NMR (200 MHz, DMSO-d_6, 20 °C) δ 1.44 (filled-in doublet, $J_{HP_{app}}$ = 6.0 Hz, 12 H, P-Me), 1.94 (d, $^2J_{HP}$ = 16.2 Hz, 4 H, P-CH_2); $^{31}P\{^1H\}$ NMR (DMSO-d_6, 20 °C) δ 48.3; $^{13}C\{^1H\}$ NMR (DMSO-d_6, 20 °C) δ 11.5 (pseudotriplet, $J_{CP_{app}}$ = 14 Hz, P-Me), 25.9 (pseudotriplet, $J_{CP_{app}}$ = 24 Hz, P-CH_2), 250.3 (s, C=S);

IR (Nujol mull) ν(C=S) 1035 s. Anal. Calcd for $C_7H_{18}P_2S_3Ni$: C, 26.3; H, 5.6; S, 30.1. Found: C, 26.7, H, 5.1; S, 30.0.

By using $^{13}CS_2$, a sample of **5*** was prepared: IR (Nujol mull) ν(^{13}C=S) 1000 s.

Thioketone **6**: ^{1}H NMR (200 MHz, C_6D_6, 20 °C) δ 0.97 (s, 6 H, CMe_2), 2.80 (s, 2 H, CH_2), 6.9–8.0 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 28.7 (C*Me*$_2$), 42.2 (CMe_2), 65.7 (CH_2), 123.4, 123.7, 127.7, 134.6 (aromatic C–H carbons), 144.6, 162.4 (aromatic quaternary carbons), 244.1 (C=S); IR (neat film) ν(C=S) 1320 s, 1290 s; MS *m/e* 176. Anal. Calcd for $C_{11}H_{12}S$: C, 74.9; H, 6.9; S, 18.2. Found; C, 75.0; H, 7.0; S, 17.8.

Selected spectroscopic data for ^{13}C-enriched **6***: ^{1}H NMR (200 MHz, C_6D_6, 20 °C) δ 2.80 (d, $^2J_{HC}$ = 6.3 Hz, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 65.7 (d, $^1J_{CC}$ = 35 Hz, CH_2), 144.6 (d, $^1J_{CC}$ = 50 Hz, C_{ar}-*C(=S)); IR (neat film) ν(^{13}C=S) 1300 s, 1280 s.

Reaction of 4 with Br$_2$. To a stirred solution of **4** (0.42 g, 1 mmol) in CH_2Cl_2 (30 mL) cooled to −60 °C was added 10 mL of a 0.1 M Br_2 solution in CH_2Cl_2 *via* canula. The resulting yellow suspension was stirred for 1 h at room temperature and the precipitate $NiBr_2$(dmpe) filtered. The filtrate was taken to dryness and the residue extracted with Et_2O. Repetition of this step using petroleum ether as the solvent furnished a final solution of pure **6**.

A similar procedure using an acetone–water mixture a solvent was followed for the reaction of **4** with HCl. The evolved SH_2 was clearly identified by its characteristic unpleasant odor. $NiCl_2$(dmpe) and **6** were obtained in quantitative yield.

Reaction of (bipy)Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$) (1c) with Excess CS$_2$. A representative experiment was as follows. Complex **1c** (0.17 g, 0.5 mmol) was dissolved in 25 mL of acetone, and the resulting dark blue solution was titrated at room temperature with a 1 M solution of CS_2 in toluene, with stirring, until the original color was completely discharged (an excess). The mixture was stirred overnight and then filtered. The filtrate was evaporated *in vacuo* and the oily residue taken up in petroleum ether. Evaporation of this red-purple solution furnished an oil which slowly crystallized in the refrigerator. The resulting red needles were identified by IR and NMR spectroscopies as the dithiolactone **2**: yield, 70%.

In some experiments, and by leaving the reaction mixture undisturbed, a brown microcrystalline material with an IR spectrum which matched that corresponding to an authenticated sample of (bipy)Ni(CS_2)[21] could be obtained. The microanalytical data also agreed with this composition.

Reaction of (Me$_3$P)$_2$Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$) (1a) with PhNCS. NMR monitoring of this reaction revealed that the inserted product ($Me_3P)_2Ni(CH_2CMe_2$-*o*-C_6H_4C(=NPh)S) (**E**) was formed quantitatively at −80 °C. The following method allows the isolation of crude **E** as a solid material. A cold (−90 °C) solution of the metalacycle **1a** (0.34 g, 1 mmol) in Et_2O (15 mL) was treated with 1 mL of a 1 M PhNCS solution in toluene. After the solution was stirred for a few minutes at this temperature, an orange material precipitated. The resulting mixture was filtered and the crude product washed with Et_2O at −40 °C and dried *in vacuo* at this temperature: yield, 75%. Compound **E** is unstable both in the solid state and in solution at room temperature: $^{31}P\{^1H\}$ NMR (CD_2Cl_2 −80 °C) AX spin system, δ_A = −14.5, δ_X = −1.2, $^2J_{AX}$ = 28 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 14.5 (d, $^1J_{CP}$ = 22 Hz, PMe_3), 16.4 (dd, $^1J_{CP}$ = 28 Hz, $^3J_{CP}$ = 4 Hz, PMe_3), 31.8, 42.4 (C*Me*$_2$), 33.7 (dd, $^2J_{CP}$ = 68, 21 Hz, Ni-CH_2), 120–130 (aromatic C–H carbons), 146.1, 146.8, 153.6 (s, aromatic quaternary carbons), 179.7 (d, $^3J_{CP}$ = 12 Hz, C=N). As described in the Results section, this compound readily forms a tris(trimethylphosphine) species, **F**, in the presence of excess of PMe_3 at low temperatures: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) AMX spin system, δ_A = −35.8, δ_M = −11.6, δ_X = −6.7, $^2J_{AM}$ = 193, $^2J_{MX}$ = 41 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90 °C) δ 183.6 (d, $^3J_{CP}$ = 21 Hz, C=N).

If a solution of complex **E** is allowed to decompose completely at 20 °C, low yields (ca. 35%) of the imino thioether **7** could be obtained after workup. Compound **7** was purified by crystallization from petroleum ether: ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.47 (s, CMe_2), 2.92 (s, CH_2), 6.9–8.2 (aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 28.3 (C*Me*$_2$), 34.2 (CMe_2), 39.9 (CH_2), 119.8, 124.0, 124.4, 126.7, 127.4, 129.1, 131.2 (2:1:1:1:1:2:1 ratio, aromatic C–H carbons), 131.7, 146.4, 151.2 (aromatic quaternary carbons), 160.9 (C=N); IR (Nujol mull) ν(C=N) 1575 s. Anal. Calcd for $C_{17}H_{17}NS$: C, 76.4; H, 6.4; N, 5.2. Found: C, 76.2; H, 6.4; N, 5.2.

Synthesis of (Me$_3$P)$_2$Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$C(=O)NPh) (8). To a stirred solution of **1a** (0.34 g, 1 mmol) in Et_2O (20 mL) was added 110 µL (1 mmol) of PhNCO. In a few minutes complex **8** started to precipitate as a yellow microcrystalline solid. The mixture was stirred for an additional 3-h period to complete the precipitation. Filtration, washing with Et_2O, and drying furnished the crude product in 75% yield. The analytical sample was crystallized from CH_2Cl_2–toluene mixtures: ^{1}H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 0.89 (d, $^2J_{HP}$ = 7.2 Hz, 9 H, PMe_3), 1.30 (d, $^2J_{HP}$ = 9.0 Hz, 9 H, PMe_3), 1.36, 1.40 (s, 3 H and 3 H, CMe_2), 0.87 (dd, $^3J_{HP}$ = 28.8 Hz, $^2J_{HH}$ = 9.0 Hz, 1 H, C*H*$_A$H$_B$), 1.81 (dd, $^3J_{HP}$ = 8.5 Hz, 1 H, CH$_A$*H*$_B$), 6.8–8.8 (m aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = −11.5, δ_X = −2.9, $^2J_{AX}$ = 16 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 14.7 (d, $^1J_{CP}$ = 15 Hz, PMe_3), 16.1 (dd, $^1J_{CP}$ = 29 Hz, $^3J_{CP}$ = 4 Hz, PMe_3), 31.4 (dd, $^2J_{CP}$ = 65, 27 Hz, Ni-CH_2), 33.3, 34.8 (s, C*Me*$_2$), 38.8 (s, CMe_2), 119.0–128.0 (aromatic C–H carbons), 143.3, 146.8, 149.6 (s, aromatic quaternary carbons), 171.0 (s, C=O); IR (Nujol mull) complex pattern at 1605–1555 cm^{-1}. Anal. Calcd for $C_{23}H_{35}NOP_2Ni$: C, 59.7; H, 7.6; N, 3.0. Found: C, 58.9; H, 7.9; N, 3.1.

The tris(trimethylphosphine) species **G**, formed when complex **8** is reacted with an excess of PMe_3 at low temperatures, is a fluxional species even at −80 °C: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ −10.0 (br s, 2 PMe_3), −1.7 (br s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 171.1 (s, C=O).

Synthesis of (Me$_3$P)$_2$Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$C(=NC$_6$H$_4$-*p*-Me)NC$_6$H$_4$-*p*-Me) (9). This complex was prepared according to a procedure very similar to that described for **8**. As **9** is a more soluble species, the filtration step was carried out at −30 °C. The analytical sample was recrystallized from CH_2Cl_2-CH_3COCH_3 as yellow prisms: ^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C) δ 0.96 (d, $^2J_{HP}$ = 6.9 Hz, 9 H, PMe_3), 1.15 (d, $^2J_{HP}$ = 8.0 Hz, 9 H, PMe_3), 1.46, 1.63 (s, 3 H and 3 H, CMe_2), 0.77 (dd, $^3J_{HP}$ = 28.7 Hz, $^2J_{HH}$ = 8.7 Hz, 1 H, C*H*$_A$H$_B$), 1.68 (t, $^3J_{HP}$ = 8.3 Hz, 1 H, CH$_A$*H*$_B$), 2.18, 2.31 (s, 3 H and 3 H, 2 Ar-*Me*), 6.8–8.6 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = −12.5, δ_X = −4.9, $^2J_{AX}$ = 14.5 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 15.4 (d, $^1J_{CP}$ = 18 Hz, PMe_3), 16.4 (dd, $^1J_{CP}$ = 29 Hz, $^3J_{CP}$ = 4 Hz, PMe_3), 20.6, 20.7 (s, C_{ar}-*Me*), 31.4 (dd, $^2J_{CP}$ = 65 Hz, 27 Hz, Ni-CH_2), 34.1, 34.2 (s, C*Me*$_2$), 39.6 (d, $^3J_{CP}$ = 3 Hz, CMe_2), 122–131 (aromatic C–H carbons), 127.2, 138.1, 149.0, 149.4, 151.5 (s, aromatic quaternary carbons), 159.5 (s, C=N); IR (Nujol mull) complex pattern at 1540–1450 cm^{-1}. Anal. Calcd for $C_{31}H_{44}N_2P_2Ni$: C, 65.8; H, 7.8; N, 4.9. Found: C, 64.5; H, 8.1; N, 4.8.

Synthesis of (PMe$_3$)(CNBu^t)Ni(CH$_2$CMe$_2$-*o*-C$_6$H$_4$) (10). CNBu^t (1 mL of a 1 M Et_2O solution) was added to a stirred, cold (−60 °C) solution of **1a** (0.34 g, 1 mmol) in Et_2O (15 mL). The resulting mixture was allowed to reach room temperature, and the volatiles were removed under vacuum. The yellow residue was washed with cold petroleum ether and dried. The yield of crude product was quantitative. The analytical sample was crystallized from Et_2O–petroleum ether mixtures: ^{1}H NMR (200 MHz, C_6D_6, 20 °C) δ 0.96 (d, $^2J_{HP}$ = 7.4 Hz, 9 H, PMe_3), 0.99 (s, 9 H, CMe_3), 1.57 (s, 6 H, CMe_2), 1.60 (br s, 2 H, Ni-CH_2), 7.1–7.9 (m, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ −10.0; $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 14.8 (d, $^1J_{CP}$ = 23 Hz, PMe_3), 29.9 (s, C*Me*$_3$), 35.2 (s, C*Me*$_2$), 49.8 (s, CH_2), 50.7 (s, CMe_2), 55.7 (s, CMe_3), 121.9, 123.6, 123.7, 139.8 (s, aromatic C–H carbons), 153.0 (br s, CNBu^t), 168.0 (br s, Ni–C_{ar}), 168.8 (s, quaternary aromatic carbon); $^{13}C\{^1H\}$ NMR (CD_3COCD_3, −70 °C) δ 49.8 (d, $^2J_{CP}$ = 19 Hz, CH_2), 50.8

(d, $^3J_{CP}$ = 10 Hz, CMe_2), 124.3 (d, J_{CP} = 6 Hz, aromatic C–H carbon), 168.1 (d, $^2J_{CP}$ = 83 Hz, Ni-C$_{ar}$); IR (Nujol mull) ν(C≡N) 2120 s. Anal. Calcd for $C_{18}H_{30}NPNi$: C, 61.7; H, 8.6. Found: C, 61.7; H, 8.6.

Synthesis of $(Me_3P)_2Ni(\eta^2\text{-}S{=}CSC({=}O)CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (11a). Method a. According to a procedure already described, complex **A** (2 mmol) was prepared *in situ* at −80 °C in Et_2O (30 mL), and CO was bubbled through the resulting solution while the temperature was allowed to rise slowly. The initial dark green color changed to orange during this process, and a yellow material precipitated. The volume of the solution was reduced to 5 mL at room temperature, and the mixture was cooled to −30 °C. Complex **11a** was filtered and dried *in vacuo*: yield, 95%. The analytical sample was crystallized from toluene: ^1H NMR (200 MHz, CD_2Cl_2, 20 °C) δ 1.30 (d, $^2J_{HP}$ = 7.8 Hz, 9 H, PMe_3), 1.41 (d, $^2J_{HP}$ = 7.6 Hz, 9 H, PMe_3), 1.39, 1.42 (s, 3 H and 3 H, CMe_2), 2.23, 5.16 (d, $^2J_{HH}$ = 12.6 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.9–7.8 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −11.0 (s, 1 PMe_3), −10.5 (s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 16.7 (d, $^1J_{CP}$ = 26 Hz, PMe_3), 17.8 (d, $^1J_{CP}$ = 24 Hz, PMe_3), 29.8, 36.2 (s, CMe_2), 38.5 (s, CMe_2), 54.7 (s, CH_2), 65.0 (d, $^2J_{CP}$ = 27 Hz, C=S), 124.1, 126.0, 129.1, 132.3 (s, s, s, d, J_{CP} = 5 Hz, aromatic C–H carbons), 144.7, 149.5 (s, aromatic quaternary carbons), 208.0 (s, C=O); IR (Nujol mull) ν(C=O) 1650 s; M_w (Signer's method, CH_2Cl_2, N_2) calcd for $C_{18}H_{30}OP_2S_2Ni$ 471, found 462. Anal. Calcd for $C_{18}H_{30}OP_2S_2Ni$: C, 48.3; H, 6.7; S, 14.3. Found: C, 48.2; H, 7.0; S, 14.3.

For a $^{13}CS_2$-enriched sample, **11a***: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ −9.3 (s, 1 PMe_3), −9.2 (d, $^2J_{PC}$ = 30 Hz, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 149.5 (d, $^1J_{CC}$ = 54 Hz, $S_2{*}CC_{ar}$).

Method b. Through a solution of **1a** (0.34 g, 1 mmol) in Et_2O (20 mL), cooled at −90 °C was gently bubbled carbon monoxide for 2–3 min, the color changing to yellow after this treatment. One equivalent of CS_2 was immediately syringed onto the reaction mixture, and the system was closed and evacuated. The temperature was slowly allowed to rise while the flask was maintained under dynamic vacuum. The precipitated material was treated as in method a: yield, 60%.

Synthesis of $(Me_3P)_2Ni(\eta^2\text{-}S{=}CSC({=}NBu^t)CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (12a). According to a procedure similar to that described for synthesis of complex **11a**, the reaction of **A** with 1 equiv of $CNBu^t$ furnished complex **12a** as a yellow solid. Crystallization could be effected from Et_2O–CH_3COCH_3: yield, 80%; ^1H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 1.28 (d, $^2J_{HP}$ = 9.4 Hz, 9 H, PMe_3), 1.34 (d, $^2J_{HP}$ = 7.4 Hz, 9 H, PMe_3), 1.38, 1.42 (s, 3 H and 3 H, CMe_2), 2.14, 4.84 (d, $^2J_{HH}$ = 13.0 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.8–7.9 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −8.8 (s, 1 PMe_3), −8.5 (s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 16.3 (d, $^1J_{CP}$ = 25 Hz, PMe_3), 17.4 (d, $^1J_{CP}$ = 24 Hz, PMe_3), 28.9 (s, CMe_3), 29.3, 36.0 (s, CMe_2), 39.3 (s, CMe_2), 51.6 (s, CH_2), 123.2, 124.9, 128.4, 131.2 (s, s, s, d, J_{CP} = 5 Hz, aromatic C–H carbons), 145.3, 150.2 (s, aromatic quaternary carbons), 162.7 (s, C=N) (the C=S carbon was not observed); IR (Nujol mull) ν(C=N) 1590 s. Anal. Calcd for $C_{22}H_{39}NP_2S_2Ni$: C, 52.6; H, 7.8; S, 12.7. Found: C, 52.7; H, 7.9; S, 12.6.

Synthesis of the dmpe Derivatives 11b and 12b. The addition of 1 equiv of dmpe to room temperature solutions of **11a** and **12a** furnished the desired substituted derivatives. Complex **11b** was recrystallized from acetone as yellow plates in 80% yield, while the related compound **12b** was obtained as yellow crystals from Et_2O (yield, 90%). **11b**: ^1H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 1.40 (d, $^2J_{HP}$ = 8.8 Hz, 3 H, P-Me), 1.41 (d, $^2J_{HP}$ = 8.5 Hz, 3 H, P-Me), 1.50 (d, $^2J_{HP}$ = 8.6 Hz, 3 H, P-Me), 1.53 (d, $^2J_{HP}$ = 8.4 Hz, 3 H, P-Me), 1.37, 1.39 (s, 3 H and 3 H, CMe_2), 1.90 (m, P-CH_2), 2.15, 5.41 (d, $^2J_{HH}$ = 12.6 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.9–7.6 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = 29.8, δ_X = 36.2, $^2J_{AX}$ = 17 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 12–15 (m, P-Me), 26.0 (dd, $^1J_{CP}$ = 28 Hz, $^2J_{CP}$ = 14 Hz, P-CH_2), 29.5 (dd, $^1J_{CP}$ = 21 Hz, $^2J_{CP}$ = 18 Hz, P-CH_2), 29.9, 35.7 (s, CMe_2), 38.1 (s, CMe_2), 54.7 (s, $C({=}O)CH_2$), 123.3, 124.9, 128.6, 131.2 (s, s, s, t, J_{CP} = 5 Hz, aromatic C–H carbons), 145.3, 150.2, (d, J_{CP} = 6, 4 Hz, aromatic quaternary carbons), 208.8 (dd, $^4J_{CP}$ = 12, 7 Hz, C=O). The C=S carbon was not observed; IR (Nujol mull) ν(C=O) 1640 s. **12b**: ^1H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 1.35 (d, $^2J_{HP}$ = 10 Hz, 3 H, P-Me), 1.45 (d, $^2J_{HP}$ = 9.5 Hz, 3 H, P-Me), 1.49 (d, $^2J_{HP}$ = 8.6 Hz, 3 H, P-Me), 1.50 (d, $^2J_{HP}$ = 8.2 Hz, 3 H, P-Me), 1.30, 1.38 (s, 3 H and 3 H, CMe_2), 1.90 (m, P-CH_2), 2.14, 5.07 (d, $^2J_{HH}$ = 12.8 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.6–7.6 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) AX spin system, δ_A = 29.3, δ_X = 35.0, $^2J_{AX}$ = 20 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 13–15 (m, P-Me), 27.0 (dd, $^1J_{CP}$ = 29 Hz, $^2J_{CP}$ = 13 Hz, P-CH_2), 29.0 (dd, $^1J_{CP}$ = 31 Hz, $^4J_{CP}$ = 12 Hz, P-CH_2), 28.7 (s, CMe_3), 29.4, 35.7 (s, CMe_2), 39.0 (s, CMe_2), 50.7 (s, $C({=}NR)CH_2$), 54.3 (s, CMe_3), 123.3, 124.9, 128.5, 131.1 (s, s, s, dd, J_{CP} = 4, 3 Hz, aromatic C–H carbons), 145.2, 150.8 (d, J_{CP} = 4, 3 Hz, aromatic quaternary carbons), 163.4 (t, $^4J_{CP}$ = 6 Hz, C=N) (the C=S carbon was not observed); IR (Nujol mull) ν(C=N) 1610 s. Anal. Calcd for $C_{22}H_{37}NP_2S_2Ni$: C, 53.0; H, 7.4; N, 2.8. Found: C, 52.9; H, 7.5; N, 2.6.

Reaction of Complex 11b with Br$_2$. Synthesis of the Cyclic Thione Derivative $S{=}CSC({=}O)CH_2CMe_2\text{-}o\text{-}C_6H_4$ (13). To a cooled (−60 °C) solution of complex **11b** (0.35 g, 0.8 mmol) in Et_2O (20 mL) was added, with stirring, 1 equiv of Br_2 (8 mL of a 1 M solution in CH_2Cl_2). A yellow precipitate of $NiBr_2$(dmpe) was immediately formed. After the solution was stirred for 10 min at room temperature, the resulting mixture was filtered and the filtrate taken to dryness. The residue was extracted with petroleum ether and the solvent evaporated. This cycle was repeated twice or until no more yellow $NiBr_2$(dmpe) remained. Compound **13** was isolated as a blue, very unstable, oil: yield, 60%, ^1H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.09 (s, 6 H, CMe_2), 2.83 (s, 2 H, CH_2), 7.0–7.8 (m, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 30.7 (CMe_2), 37.1 (CMe_2), 58.6 (CH_2), 126.4, 126.8, 131.7, 132.1 (aromatic C–H carbons), 142.2, 148.3 (aromatic quaternary carbons), 196.4 (C=O), 231.3 (C=S); IR (Neat film) ν(C=O) 1680 s, ν(C=S) 1030 s; MS *m/e* 236.

Reaction of Complex 12b with Br$_2$. Synthesis of $S{=}CSC({=}NBu^t)CH_2CMe_2\text{-}o\text{-}C_6H_4$ (14). According to the method described above for the synthesis of **13**, the related cyclic compound **14** was obtained as red crystals in 70% yield, mp 61–64 °C: ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 1.09 (s, 9 H, CMe_3), 1.26 (s, 6 H, CMe_2), 2.87 (s, 2 H, CH_2), 6.9–7.1 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 29.6 (CMe_3), 31.2 (CMe_2), 37.7 (CMe_2), 57.4 (CMe_3), 60.4 (CH_2), 125.6, 126.3, 130.5, 130.8 (aromatic C–H carbons), 142.3, 148.5 (aromatic quaternary carbons); IR (Nujol mull) ν(C=N) 1644 s, 1629 s, ν(C=S) 1021 s; MS *m/e* 291. Anal. Calcd for $C_{16}H_{21}NS_2$: C, 66.0; H, 7.2; N, 4.8. Found: C, 66.0; H, 7.4; N, 4.7.

Reaction of Complex D with Carbon Monoxide. Synthesis of the Bis(acyl)sulfide $O{=}CSC({=}O)CH_2CMe_2\text{-}o\text{-}C_6H_4$ (15). Complex **D** was prepared *in situ* at −90 °C by reacting the nickelacycle **1a** (0.34 g, 1 mmol) in Et_2O (30 mL) with 1 equiv of COS (0.8 mL of a 1.2 M solution in THF). The resulting dark red solution was treated with carbon monoxide and the cooling bath removed. After the solution reached room temperature, the volatiles were removed *in vacuo* and the residue dissolved in a mixture of Et_2O–petroleum ether (1:1). Filtration, concentration, and cooling at −30 °C furnished compound **15** as colorless crystals that were purified by recrystallization from a petroleum ether–Et_2O (4:1) mixture: yield, 57%, mp 69–70 °C; ^1H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.50 (s, 6 H, CMe_2), 3.13 (s, 2 H, CH_2), 7.3–7.5 (m, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 31.3 (CMe_2), 37.5 (CMe_2), 59.0 (CH_2), 127.2, 127.6, 130.0, 132.7 (aromatic C–H carbons), 139.1, 145.5 (aromatic quaternary carbons), 190.5 (C_{ar}-C=O), 195.5 (CH_2-C=O, gated spectrum: t, $^2J_{CH}$ = 6 Hz); IR (Nujol mull) ν(C=O) 1710 s, 1660 s; MS *m/e* 220. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.4; H, 5.5. Found: C, 64.9; H, 5.6.

Synthesis of PhN=CSC(=O)CH_2CMe_2-*o*-C_6H_4 (16). The title compound was obtained from complex **E** and CO according to a procedure similar to that presented above for the synthesis of **15**. Compound **16** gave colorless crystals from petroleum ether–Et_2O mixtures (3:1): mp 130–132 °C, yield, 93%; ^1H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.07 (s, 6 H, CMe_2), 2.85 (s, 2 H, CH_2), 6.5–7.1 (m, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 32.2 (C*Me*$_2$), 38.9 (CMe_2), 57.5 (CH_2), 119.7, 125.4, 126.8, 129.0, 129.2, 130.4, 130.7 (2:1:1:1:2:1:1 ratio, aromatic C–H carbons), 139.4, 144.4, 149.5 (aromatic quaternary carbons), 157.5 (C=N, gated spectrum: d, $^3J_{CH}$ = 4 Hz), 195.2 (C=O, gated spectrum: t, $^3J_{CH}$ = 5 Hz); IR (Nujol mull) ν(C=O) 1675 s, ν(C=N) 1590 s; MS *m/e* 295. Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.2; H, 5.8; N, 4.7. Found: C, 72.9; H, 5.9; N, 4.6.

Synthesis of the η^2-Iminoacyl Complexes 17 and 18. Complex **D** (1 mmol) was generated *in situ* as described in the synthesis of **15**. At -80 °C, 0.11 mL (1 mmol) of $CNBu^t$ was added *via* syringe, and the appearance of an orange precipitate was noticed. This solid completely dissolved upon increasing the temperature, and at 0 °C, a pale yellow solution was obtained. The solution was taken to dryness and the residue crystallized from a 4:1 Et_2O–petroleum ether mixture. The yield of orange **17** was 62%: ^1H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 1.19 (s, 9 H, CMe_3), 1.25 (d, $^2J_{HP}$ = 7.3 Hz, 9 H, PMe_3), 1.52, 1.83 (s, 3 H and 3 H, CMe_2), 2.68, 2.78 (AB spin system, $^2J_{HH}$ = 17.5 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.8–7.5 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ -13.5; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -70 °C) δ 15.2 (d, $^1J_{CP}$ = 24 Hz, PMe_3), 27.5, 31.4 (s, C*Me*$_2$), 28.9 (s, C*Me*$_3$), 38.3 (s, CMe_2), 40.8 (s, CH_2), 46.2 (s, CMe_3), 125.4, 126.1, 126.2, 126.7 (s, aromatic C–H carbons), 176.2 (d, $^2J_{CP}$ = 63 Hz, C=N), 216.2 (d, $^3J_{CP}$ = 17 Hz, C=O); IR (Nujol mull) ν(C=N) 1725 s, ν(C=O) 1600 s. Anal. Calcd for $C_{19}H_{30}NOPSNi$: C, 55.9; H, 7.4; N, 3.4. Found: C, 55.4; H, 7.5; N, 3.4.

A similar procedure allowed the synthesis of the η^2-iminoacyl complex **18**. In this case, after the reaction mixture was warmed at 0 °C, the volume was reduced to 10 mL and the solution cooled to -30 °C. A quantitative yield of orange crystals was obtained: ^1H NMR (200 MHz, CD_3COCD_3, 20 °C) δ 1.15 (d, $^2J_{HP}$ = 7.3 Hz, 9 H, PMe_3), 1.19 (s, 9 H, CMe_3), 1.58, 2.02 (s, 3 H and 3 H, CMe_2), 2.79, 2.89 (AB spin system $^2J_{HH}$ = 17.1 Hz, 1 H and 1 H, diastereotopic CH_2 protons), 6.8–7.5 (m, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ -13.9; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -70 °C) δ 15.3 (d, $^1J_{CP}$ = 24 Hz, PMe_3), 28.6, 31.7 (s, C*Me*$_2$), 29.0, (s, C*Me*$_3$), 39.0 (s, CMe_2), 41.9 (s, CH_2), 44.0 (s, CMe_3), 119–130 (aromatic C–H carbons), 139.6, 147.5, 153.1 (s, aromatic quaternary carbons), 176.6 (d, $^2J_{CP}$ = 64 Hz, *C*=NBu^t), 182.0 (d, $^3J_{CP}$ = 18 Hz, *C*=NPh); IR (Nujol mull) ν(C=NBu^t) 1720 s, ν(C=NPh) 1570 s; M_w (Signer's method, CH_2Cl_2, N_2) calcd for $C_{25}H_{35}N_2PSNi$ 485, found 471. Anal. Calcd for $C_{25}H_{35}N_2PSNi$: C, 61.9; H, 7.2; N, 6.6. Found: C, 62.5; H, 7.3; N, 6.4.

Reaction of the Iminoacyl Complexes 17 and 18 with CO. Synthesis of the Heterocycles X=CSC(=NBu^t)CH_2CMe_2-*o*-C_6H_4 (X = O, 19; X = NPh, 20). Carbon monoxide was bubbled at room temperature through a solution of complex **17** (0.3 g, 0.6 mmol) in 25 mL of Et_2O–CH_3COCH_3 (2:1) for a few minutes. The resulting colorless solution was then taken to dryness and the residue heated (40 °C) under vacuum to eliminate the volatile $Ni(CO)_3(PMe_3)$. A cycle of extraction with petroleum ether, filtration, and evaporation was repeated three times. The final solution was concentrated to a volume of ca. 3 mL and cooled to -30 °C to give compound **19** as large colorless crystals: mp 60–64 °C, yield, 80%; ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 1.15 (s, 9 H, CMe_3), 1.45 (s, 6 H, CMe_2), 3.41 (s, 2 H, CH_2), 6.9–7.8 (m, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 29.1 (C*Me*$_3$), 31.8 (C*Me*$_2$), 38.0 (CMe_2), 57.1 (CMe_3), 59.1 (CH_2), 126.5, 126.9, 128.9, 131.3 (aromatic C–H carbons), 140.2, 145.5 (aromatic quaternary carbons); IR (Nujol mull) ν(C=O) 1670 s, ν(C=N) 1640 s, MS *m/e* 275. Anal. Calcd for $C_{16}H_{21}NOS$: C, 69.8; H, 7.6; N, 5.1. Found: C, 69.7; H, 7.6; N, 5.0.

Table 5. Fractional Coordinates for 3a

atom	*X/A*	*Y/B*	*Z/C*	U_{eq}, Å^2
Ni	0.3498(1)	0.4026(1)	0.4299(1)	45(0)
P1	0.4208(1)	0.3698(3)	0.3419(2)	52(1)
P2	0.3365(1)	0.1957(3)	0.4880(2)	53(1)
S1	0.3260(1)	0.6248(3)	0.4064(2)	64(1)
S2	0.3275(1)	0.5408(4)	0.6161(2)	82(1)
O	0.5000(0)	0.5000(0)	0.0000(0)	140(6)
C1	0.2889(5)	0.5198(10)	0.4813(6)	49(3)
C2	0.2628(8)	0.6730(21)	0.6262(12)	135(14)
C3	0.1902(5)	0.6243(12)	0.5957(7)	59(4)
C4	0.1634(5)	0.5440(10)	0.4936(6)	48(3)
C5	0.2091(5)	0.5004(9)	0.4424(6)	43(3)
C6	0.1800(5)	0.4293(10)	0.3486(7)	55(4)
C7	0.1077(6)	0.4019(12)	0.3078(7)	65(4)
C8	0.0639(6)	0.4442(14)	0.3587(9)	82(5)
C9	0.0908(5)	0.5156(14)	0.4497(8)	70(5)
C10	0.1437(9)	0.7457(19)	0.5998(13)	131(0)
C11	0.1864(9)	0.5248(19)	0.6797(13)	131(0)
C12	0.3706(6)	0.3336(15)	0.2098(8)	86(6)
C13	0.4902(6)	0.2333(13)	0.3711(10)	82(6)
C14	0.4741(6)	0.5244(12)	0.3355(9)	76(5)
C15	0.2613(7)	0.1634(13)	0.5315(9)	90(6)
C16	0.4093(7)	0.1366(14)	0.5979(10)	98(6)
C17	0.3245(8)	0.0474(13)	0.4008(9)	93(7)
C18	0.5513(9)	0.4002(21)	0.0361(14)	139(0)
C19	0.5783(9)	0.3304(20)	0.1106(14)	137(0)

Table 6. Fractional Coordinates for 4

atom	*X/A*	*Y/B*	*Z/C*	U_{eq},[a] Å^2
Ni	0.022 13(5)	0.374 49(4)	0.911 90(2)	439(2)
P1	–0.145 77(10)	0.375 35(10)	0.880 02(5)	565(4)
P2	–0.047 24(10)	0.317 95(9)	0.984 35(5)	504(4)
S1	0.191 92(9)	0.391 18(8)	0.942 19(4)	458(4)
S2	0.105 33(10)	0.426 10(9)	0.840 52(5)	510(4)
C1	0.240 24(34)	0.432 89(28)	0.876 91(16)	390(13)
C2	0.294 57(39)	0.531 67(29)	0.878 04(19)	492(15)
C3	0.380 70(39)	0.535 99(30)	0.832 05(19)	486(15)
C4	0.410 44(35)	0.431 76(29)	0.826 51(17)	418(14)
C5	0.330 67(34)	0.375 12(29)	0.850 81(16)	387(13)
C6	0.338 69(41)	0.276 89(29)	0.847 94(19)	518(16)
C7	0.427 90(46)	0.236 49(34)	0.820 48(21)	614(19)
C8	0.507 23(42)	0.292 39(36)	0.796 36(20)	606(18)
C9	0.499 71(39)	0.391 40(34)	0.798 83(19)	562(17)
C10	0.481 82(48)	0.598 43(36)	0.845 01(25)	802(22)
C11	0.326 09(51)	0.570 76(36)	0.780 19(21)	727(21)
C12	–0.175 24(48)	0.322 18(49)	0.816 30(24)	879(25)
C13	–0.205 45(50)	0.492 21(45)	0.874 00(27)	885(25)
C14	–0.239 90(44)	0.315 46(46)	0.927 21(24)	811(23)
C15	–0.199 88(42)	0.334 35(40)	0.983 51(22)	696(20)
C16	0.000 61(50)	0.365 96(39)	1.046 78(19)	730(20)
C17	–0.028 84(46)	0.191 17(35)	0.992 25(23)	702(20)

[a] $U_{eq} = (^1/_3)\sum(U_{ij}a_i^{*}\cdot a_j^{*}\cdot \mathbf{a}_i\cdot \mathbf{a}_j \cos(\mathbf{a}_i\cdot \mathbf{a}_j)) \times 10^4$.

According to a similar procedure but using complex **18** as the starting material, the bis(imino) compound **20** was obtained. In this case, the isolation of the pure product was facilitated by treatment of the crude petroleum ether solution with CS_2 to precipitate soluble nickel carbonyls. Final purification was achieved by flash chromatography using petroleum ether–Bu^t-OMe (24:1) as eluent: yield of the pale yellow oily product, 70%; ^1H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.18 (s, 9 H, CMe_3), 1.47 (s, 6 H, CMe_2), 3.12 (s, 2 H, CH_2), 6.9–7.5 (m, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 28.7 (C*Me*$_3$), 32.2 (C*Me*$_2$), 39.7 (CMe_2), 56.4 (CH_2), 56.6 (CMe_3), 119.7, 124.8, 126.3, 128.4, 128.8, 129.7 (2:1:1:1:2:2 ratio, aromatic C–H carbons), 140.3, 145.6, 150.2 (aromatic quaternary carbons), 150.0, 160.5 (C=N); IR (neat film) ν(C=N) 1635 s, 1590 s, MS *m/e* 350.

Synthesis of X=CN(Ar)C(=O)CH_2CMe_2-*o*-C_6H_4 Derivatives (Ar = Ph, X = O, 21; Ar = C_6H_4-*p*-Me, X = C_6H_4-*p*-Me, 22). Complex **8** (0.42 g, 0.9 mmol) was dissolved in 30 mL of THF, and through this solution carbon monoxide was bubbled at room temperature for 5 min. The now pale yellow mixture was evaporated under reduced pressure and the residue extracted with Et_2O. The solution was filtered, concentrated, and kept at

Table 7. Fractional Coordinates for 5

atom	*X/A*	*Y/B*	*Z/C*	U_{eq},[a] Å^2
Ni	0.75184(4)	0.06380(7)	0.08997(4)	333(1)
P1	0.85181(7)	0.25782(15)	0.15068(8)	344(3)
P2	0.64556(7)	0.22098(16)	0.15785(9)	369(3)
S1	0.85014(8)	–0.09609(19)	0.00218(10)	540(4)
S2	0.65714(9)	–0.13778(18)	0.01696(11)	523(4)
S3	0.75243(13)	–0.37109(20)	–0.13671(12)	703(5)
C1	0.75330(34)	–0.21468(58)	–0.04526(34)	443(14)
C11	0.93694(39)	0.17073(83)	0.24870(43)	672(20)
C12	0.92331(34)	0.36379(75)	0.05698(37)	533(16)
C13	0.79129(35)	0.44186(73)	0.21087(43)	597(18)
C21	0.58554(35)	0.36091(75)	0.05975(41)	576(17)
C22	0.55059(34)	0.11440(78)	0.22228(42)	582(18)
C23	0.70057(34)	0.37215(78)	0.25476(41)	594(18)

[a] $U_{eq} = (^1/_3)\sum(U_{ij}a_i^*\cdot a_j^*\cdot \mathbf{a}_i\cdot \mathbf{a}_j \cos(\mathbf{a}_i\cdot \mathbf{a}_j)) \times 10^4$.

–30 °C. Compound **21** separated as colorless crystals: mp 119 °C, 80% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.56 (s, 6 H, CMe_2), 3.06 (s, 2 H, CH_2), 7.1–8.0 (m, aromatics); ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ 29.4 (C*Me*$_2$), 35.3 (CMe_2), 52.0 (CH_2), 124.8, 127.0, 128.1, 129.3, 132.7, 134.1 (1:1:3:2:1:1 ratio, aromatic C–H carbons), 132.0, 138.9, 147.2 (aromatic quaternary carbons), 174.2, 176.0 (C=O); IR (Nujol mull) ν(C=O) 1700 s, 1660 s, 1650 s, MS *m/e* 279. Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.4; H, 6.1; N, 5.0. Found: C, 77.5; H, 6.0; N, 4.8.

A solution of complex **9** (0.28 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was pressurized with CO (3 atm) and stirred for 4 h at room temperature. The resulting dark mixture was taken to dryness, extracted with 30 mL of a petroleum ether–Et_2O mixture (3:1), and filtered. The orange filtrate was concentrated *in vacuo* to a final volume of 3 mL and kept in the refrigerator. The crystalline product thus obtained was recrystallized from a petroleum ether–Et_2O mixture to give a 50% yield of colorless crystals: mp 159–161 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) δ 1.48 (s, 6 H, CMe_2), 2.16, 2.25 (s, 3 H and 3 H, 2 ArMe), 3.05 (br s, 2 H, CH_2), 6.5–7.9 (m, aromatics); ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ 20.9, 21.0 (2 Ar*Me*), 31.9 (br s, C*Me*$_2$), 37.4 (CMe_2), 49.0 (CH_2), 119.3, 125.0, 126.7, 128.4, 128.7, 129.1, 130.5, 131.0 (2:2:1:1:2:2:1:1 ratio, aromatic C–H carbons); 133.7, 135.3, 135.6, 136.1, 144.8, 146.4 (aromatic quatenary carbons), 157.3 (C=N), 168.1 (C=O); IR (Nujol mull) ν(C=O) 1690 s, 1640 s, ν(C=N) 1510 s, 1505 s, MS *m/e* 381 ($M^+ - 1$).

Reaction of *trans*-NiBr(PMe_3)$_2$(COPh) with *trans*-NiBr(PMe_3)$_2$Me. Equimolecular amounts of these complexes[58,59] were dissolved at room temperature in CD_2Cl_2. NMR monitoring of the reaction mixture indicated complete transformation to *trans*-NiBr(PMe_3)$_2$Ph[58] and *trans*-NiBr(PMe_3)$_2$(COMe).[60]

X-ray Structure Determination of Compounds 3a, 4, and 5. A summary of the fundamental crystal data are given in Table 4. Appropriate single crystals were coated with epoxy resin and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, P, and S were taken from ref 61. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[62] was applied at the end of the isotropic refinement. The refinement involved anisotropic thermal parameters for the non-hydrogen atoms. Final refinement with fixed isotropic factors and coordinates for H atoms gave R_F = 0.035 and $R(\omega)_F$ = 0.035 (**4**) and R_F = 0.035 and $R(\omega)_F$ = 0.039 (**5**). For **3a**, the methyl carbon atoms and the ether molecule were refined isotropically, and the hydrogens were included in the refinement with fixed contributions at their calculated positions. Some nonresolvable disorder from thermal motion was found in the ether molecule. Final mixed full-matrix least-squares refinement gave R_F = 0.071 and $R(\omega)_F$ = 0.078. Most of the calculation were carried out with the X-ray 80 system.[63] Fractional coordinates for **3a**, **4**, and **5** are given in Tables 5–7, respectively.

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Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **3a**, **4**, and **5** (6 pages). Ordering information is given on any current masthead page.

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