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Reactions of Benzyne−Nickel(0) Complexes with Thioalkynes: Preparation and Coordination of Polydentate Thioethers Containing a 2,3-Naphthylene Backbone

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Double insertion reactions of the thioalkynes MeC≡CS-*p*-Tol and $(MeC{\equiv}CSCH_2CH_2)_2S$ with benzyne−nickel(0) complexes have been used to prepare the 2,3-di(thioether) naphthalene species 2,3-$(p\text{-TolS})_2$-1,4-$Me_2C_{10}H_4$ (**4**) and the 2,3-naphthotrithiacyclononane 2,3-$S(C_2H_4S)_2$-1,4-$Me_2C_{10}H_4$ (**5**), respectively. Both naphthothioethers act as ligands toward ruthenium, and the products of the reactions of **4** and **5** with $[RuCl_2(PPh_3)_4]$, viz., $[(PPh_3)\{2,3\text{-}(p\text{-TolS})_2\text{-}1,4\text{-}Me_2C_{10}H_4\}Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**6**) and $[RuCl_2\{2,3\text{-}S(C_2H_4S)_2\text{-}1,4\text{-}Me_2C_{10}H_4\text{-}\kappa S,S,S\}(PPh_3)]$ (**7**), have been isolated and structurally characterized by X-ray diffraction. The Ru^{II},Ru^{II} dinuclear complex **6** exhibits two successive one-electron voltametric oxidations akin to complex $[Cl(PPh_3)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_3]$, and has similar potentials.

Introduction

Macrocycles have been used extensively for their ability to coordinate metals with high selectivities. By incorporating luminescent substituents into their backbone, these compounds have proved to be sensitive ion probes, as changes in the absorption or fluorescence of the photoactive groups can be measured for very low concentrations of metal present.[1−3] Some attractive examples include macrocycles, incorporating oxygen and/or nitrogen donors, that are attached to polyaromatic species such as anthracenes (via the 9 and/or 10 positions)[4−6] or naphthalenes (via the 2 and 3 positions).[7] Sulfur-based macrocycles are also known to coordinate transition metals, and one of the most commonly used is 1,4,7-trithiocyclononane ([9]aneS_3).[8] However, they have not been applied as their nitrogen and oxygen analogues have, because the preparation of [9]aneS_3 ligands substituted with chromophores is not easily achieved.

Scheme 1

Recently, we have used the double-insertion reactions of unsymmetrical alkynes with benzyne−nickel(0) complexes to prepare naphthalenes regiospecifically substituted in the 2 and 3 positions. This was achieved with alkynes of the type MeC≡CR (R = CO_2Me, PPh_2), the former leading to a 2,3-dicarboxylato species,[9,10] while the latter formed a new kind of chelating diphosphine ligand in excellent yield (Scheme 1).[11,12] Hence, we wondered whether similar reactions with thioalkynes would show similar high regioselectivities and whether this methodology could be used to prepare naphthalene-based thioether chelating ligands. Two examples, including the generation of a [9]aneS_3-containing species, are reported here, and their coordinations to ruthenium have been explored.

Experimental Results

(i) Preparation of the Naphtho Thioethers. The benzyne−nickel(0) complex $[Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2]$ (**2**) is prepared by lithium reduction of $[NiBr(C_6H_4Br\text{-}2)(PEt_3)_2]$ (**1**).[9] Complex **2** is very reactive toward oxygen

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[†] Single-Crystal X-Ray Diffraction Unit.

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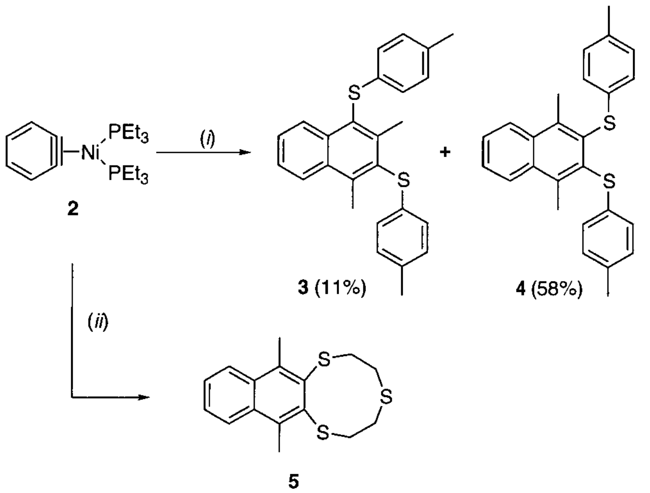
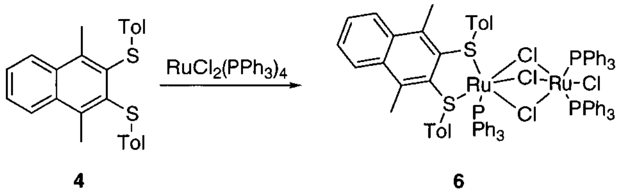
Scheme 2[a]



[a] (i) MeC≡CSC$_6$H$_4$Me-4 (2 equiv); (ii) MeC≡CSC$_2$H$_4$SC$_2$H$_4$-SC≡CMe.

Scheme 3[a]



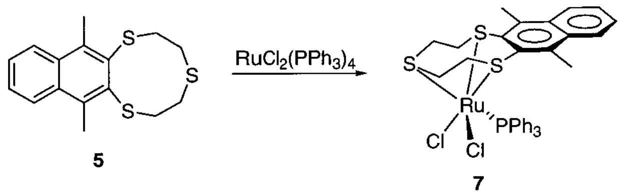
[a] Tol = *p*-MeC$_6$H$_4$.

and moisture, but isolation is not required. Double insertion reaction in situ with 2 equiv of the thioalkyne MeC≡CS-*p*-Tol at low temperature gave readily a 5.3:1 mixture of two dithioether-substituted naphthalenes in good overall yields. The minor product was unsymmetrical, as shown by its ^{1}H and ^{13}C NMR spectra, and has been assigned to 1,3-(*p*-TolS)$_2$-2,4-Me$_2$C$_{10}$H$_4$ (**3**), while the major component was a symmetrically substituted naphthalene (**4**) (Scheme 2). The compound could not be crystallized; hence it was not certain whether the two thioether groups were in the 1,4 or 2,3 positions. However, due to the electronic analogy of MeC≡CS-*p*-Tol with MeC≡CPPh$_2$, which reacts exclusively with **2** to give the product having the PPh$_2$ groups in the 2,3 positions,[11,12] **4** was assumed to be 2,3-(*p*-TolS)$_2$-1,4-Me$_2$C$_{10}$H$_4$. This formulation was confirmed crystallographically after coordination of **4** to a transition metal (see below).

Reaction of the diyne (MeC≡CSCH$_2$CH$_2$)$_2$S with **2** also occurred readily to give exclusively the trithiocyclononane species 2,3-S(C$_2$H$_4$S)$_2$-1,4-Me$_2$C$_{10}$H$_4$ (**5**) (Scheme 2), as shown by ^{1}H NMR analysis of the crude reaction mixture. Addition of exactly 1 equiv (relative to **1**) of *o*-dibromobenzene showed the yield of formation of **5** to be >90% by relative NMR integration of the aromatic protons. The purification of **5**, however, proved to be difficult, and the macrocycle seemed to decompose during chromatography. The best yield (45% overall) was obtained by fast preparative TLC separation.

(ii) Reactions of the Naphtho Thioethers with [RuCl$_2$(PPh$_3$)$_4$]. The 2,3-dithioether **4** reacted slowly with [RuCl$_2$(PPh$_3$)$_4$] at 30 °C (Scheme 3), and ^{31}P NMR monitoring of the solution showed increasing amounts of free PPh$_3$ and several signals for coordinated PPh$_3$ in the region δ_P 29−60. After 2 days, only two signals remained in a 2:1 ratio at δ_P 48.2 and 50.3, respectively, the very small value of the coupling (1.5 Hz) suggesting that the two phosphines were not located on the same metal center. The ^{1}H NMR spectrum of the isolated solid (**6**) showed a shielding of the two methyl groups in the 1,4-positions from δ_H 2.92 in **4** to 2.34 and 2.31. The presence of two CH$_3$ signals is indicative of an unsymmetrical environment around the naphthalene unit. The large molecular ion of *m*/*z* 1531 measured by FAB mass spectrometry suggested of a dimetallic species, and the formulation of **6** as a trichloro-bridged dimer, [(PPh$_3$)-{2,3-(*p*-TolS)$_2$-1,4-Me$_2$C$_{10}$H$_4$}Ru(μ-Cl$_3$)RuCl(PPh$_3$)$_2$], was confirmed by X-ray analysis (see below).

Scheme 4



The dinuclear complex **6** shows two distinct oxidations, measured by cyclic voltammetry at −60 °C: the first Ru^{II}/Ru^{III} couple appears at $E = +0.62$ V (vs Ag−AgCl) and the second one at $E = +1.44$ V. Both couples are fully consistent with diffusion-controlled reversible one-electron processes by the usual cyclic and alternative current voltammetry criteria. Above −30 °C in the electrolyte solution (0.5 M [N^{n}Bu$_4$][PF$_6$] in CH$_2$Cl$_2$), complex **6** progressively gives way to a species that is harder to oxidize, showing a characteristic reversible oxidation at $E = +0.83$ V, accompanied by an increasingly prominent irreversible oxidation near +1.4 V attributable to free Cl$^-$. The same changes are evident within minutes if **6** is added to the electrolyte mixture at room temperature. These changes are probably due to the high ionic strength of the electrolyte promoting dissociation of a chloride.

The macrocyclic ligand **5** reacts readily with [RuCl$_2$(PPh$_3$)$_4$] at room temperature to give a yellow solid that is poorly soluble in hot methylene chloride and chloroform and only slightly more soluble in 1,1,2,2-tetrachloroethane. The ^{31}P NMR spectrum of the product (**7**) (Scheme 4) contains only one signal at δ_P 33.8, which is similar to that observed for the product of the analogous reaction of 1,4,7-trithiacyclononane ([9]aneS$_3$) with [RuCl$_2$(PPh$_3$)$_3$], viz., [RuCl$_2$([9]aneS$_3$)(PPh$_3$)] (δ_P 35.0).[14] Hence, **7** is formulated as [RuCl$_2${2,3-S(C$_2$H$_4$S)$_2$-1,4-Me$_2$C$_{10}$H$_4$-κ*S*,*S*,*S*}(PPh$_3$)], the structure of which has been confirmed by X-ray diffraction analysis (see below). The ^{1}H NMR spectrum of **7** confirms that the complex contains only one PPh$_3$ group, but shows also that the complex is unsymmetrical in solution, as indicated by two distinct signals at δ_H 2.87 and 3.20 for the two naphthyl methyl groups. This is probably due to steric reasons, as a symmetrical product would have the PPh$_3$ group directly underneath the naphthalene unit (see isomers **A** vs **B** in Figure 3). For more flexible macrocycles, e.g., the larger benzyl-substituted trithiocycloundecane species *o*-C$_6$H$_4$(CH$_2$SCH$_2$CH$_2$)$_2$S, coordination to a RuCl$_2$(PPh$_3$) fragment has been reported to form a mixture of the two isomers **A** and **B** in solution.[13]

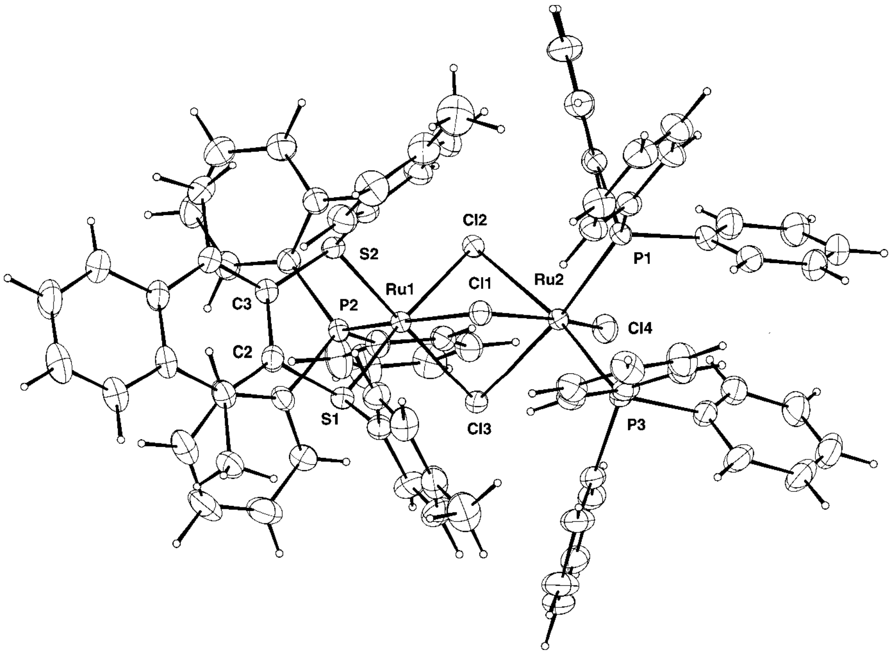


Figure 1. Molecular structure of **6** with selected atom labeling. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been drawn as circles with small radii.

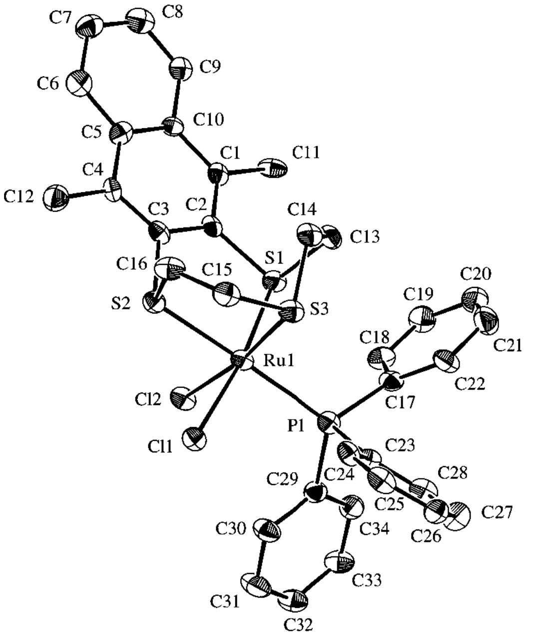


Figure 2. Molecular structure of **7** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

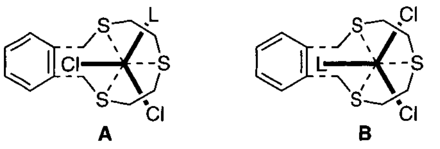


Figure 3.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Ru(1)−Cl(1)	2.4507(5)	Ru(2)−Cl(1)	2.4281(6)
Ru(1)−Cl(2)	2.4187(5)	Ru(2)−Cl(2)	2.5548(5)
Ru(1)−Cl(3)	2.4099(5)	Ru(2)−Cl(3)	2.5373(5)
Ru(1)−P(2)	2.3004(6)	Ru(2)−Cl(4)	2.3866(6)
Ru(1)−S(1)	2.2805(6)	Ru(2)−P(1)	2.2808(6)
Ru(1)−S(2)	2.2808(6)	Ru(2)−P(3)	2.2793(6)
S(1)−C(2)	1.802(2)	S(2)−C(3)	1.798(2)
Cl(1)−Ru(1)−Cl(2)	79.838(18)	Cl(1)−Ru(2)−Cl(2)	77.629(18)
Cl(1)−Ru(1)−Cl(3)	79.998(18)	Cl(1)−Ru(2)−Cl(3)	77.596(18)
Cl(2)−Ru(1)−Cl(3)	84.909(19)	P(1)−Ru(2)−Cl(4)	92.43(2)
S(2)−Ru(1)−P(2)	90.85(2)	P(3)−Ru(2)−Cl(4)	95.59(2)
S(1)−Ru(1)−S(2)	87.59(2)	P(1)−Ru(2)−P(3)	96.84(2)
Ru(1)−Cl(1)−Ru(2)	85.331(18)	Ru(1)−Cl(2)−Ru(2)	83.288(17)
Ru(1)−Cl(3)−Ru(2)	83.841(17)		

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 7

Ru(1)−Cl(1)	2.449(3)	Ru(1)−Cl(2)	2.465(2)
Ru(1)−P(1)	2.333(3)	Ru(1)−S(1)	2.275(3)
Ru(1)−S(2)	2.330(3)	Ru(1)−S(3)	2.288(3)
S(1)−C(2)	1.784(11)	S(2)−C(3)	1.83(1)
Cl(1)−Ru(1)−Cl(2)	90.85(9)	Cl(2)−Ru(1)−P(1)	94.2(1)
S(1)−Ru(1)−P(1)	95.6(1)	S(2)−Ru(1)−P(1)	176.65(11)
S(3)−Ru(1)−P(1)	92.59(11)	S(1)−Ru(1)−S(2)	87.8(1)

Molecular Structures of $[(PPh_3)\{2,3\text{-}(p\text{-}TolS)_2\text{-}1,4\text{-}Me_2C_{10}H_4\}Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (6) and $[RuCl_2\{2,3\text{-}S(C_2H_4S)_2\text{-}1,4\text{-}Me_2C_{10}H_4\text{-}\kappa S,S,S\}(PPh_3)]$ (7). The molecular geometries of **6** and **7** are shown, together with the atom labelings, in Figures 1 and 2, respectively; corresponding selected interatomic distances and angles are listed in Tables 1 and 2.

The two ruthenium atoms of the dinuclear complex **6** are in a distorted octahedral environment and are linked by three (μ-chloro) bridges. Due to the nature of this interaction, the Cl−Ru−Cl and Ru−Cl−Ru angles are all smaller than 90° (ca. 80−85°). The molecule contains a pseudo plane of symmetry that includes P(2), Ru(1), Cl(1), Ru(2), and Cl(4), and the Ru−Ru distance of 3.306 Å is within the range 3.2−3.5 Å generally reported for such Ru(μ-Cl)$_3$Ru complexes with a closed-shell d^6−d^6 configuration in which no metal−metal bonding is taking place.[14−16] The three ligands located in the external face of ruthenium atom Ru(1) are

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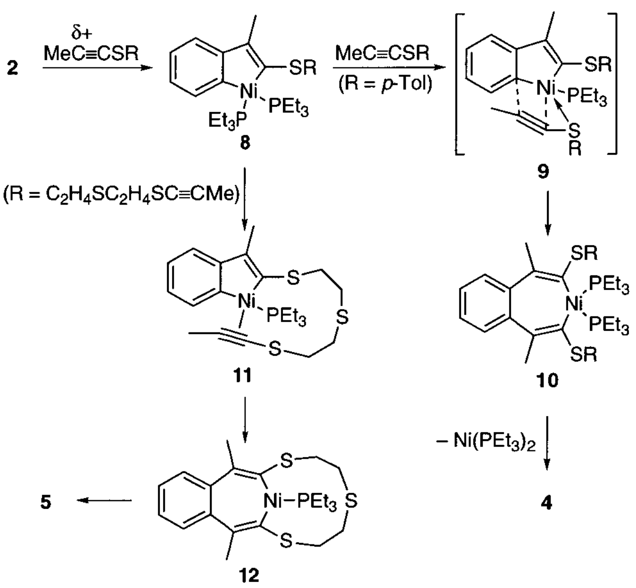
orthogonal to each other; Ru(1) is chelated by one molecule of 2,3-dithioether-substituted naphthalene (**4**), while the remaining coordination site is occupied by a PPh_3 group. The external face of the second ruthenium atom is constituted of two PPh_3 groups and one chloride with angles slightly larger than 90°, especially the P(1)−Ru(2)−P(3) one (96.84(2)°) due to the steric interaction between the two PPh_3 groups. The tri(μ-chloro) bridge is not symmetrical. The chlorine atom Cl(1) is located closer to Ru(2) than Ru(1) [Ru(1)−Cl(1) = 2.4507(5) Å vs Ru(2)−Cl(1) = 2.4281(6) Å], while Cl(2) and Cl(3) are closer to Ru(1), reflecting the strong trans-influence of the phosphine ligands. Similar lengthening of the bonds trans to phosphine groups and compression of the corresponding Cl−Ru−Cl angles have already been reported for several mixed-ligand complexes with a Ru(μ-Cl)$_3$Ru core.[14,16,17] The two Ru−S bond lengths in **6** (ca. 2.281 Å) are almost identical to the Ru−P ones and are nonexceptional when compared to those of S-bonded DMSO analogues [(dmso)$_2$ClRu(μ-Cl)$_3$Ru(dmso)$_3$] (average Ru−S bond length for the RuS_3 face = 2.268 Å)[18] or of crown-thioether complexes of ruthenium; the rare complexes having ruthenium chelated by acyclic thioethers have comparable distances.[19]

The molecular structure of **7** shows one face of the octahedral ruthenium(II) center to be coordinated to the three sulfur atoms of the trithio macrocycle, while the other three coordination sites are occupied by two chlorides and one PPh_3 group. The ruthenium atom lies in the plane of the naphthalene unit and the two arylthioether groups, as shown by the very small dihedral angle (2.22°) between the plane formed by Ru(1), S(1), and S(2) and that of the aromatic ring C(1)−C(5), C(10); this coordination geometry results in a tilt angle of 54.80° between the aromatic plane and that of the three sulfur atoms. The two Ru−S distances trans to Cl are comparable, although Ru−S(1) (2.275(3) Å) is slightly shorter than Ru−S(3) (2.288(3) Å), probably due to the increased electron density of S(1) by the adjacent aromatic ring. As expected, the bond trans to PPh_3 is longer (2.330(3) Å), but again it is slightly shorter than analogous bonds formed by coordination of the [$RuCl_2$(PPh_3)] fragment to the nonaromatic 1,4,7-trithiocyclononane macrocycle ([9]aneS_3): 2.356(2) Å for [$RuCl_2$([9]aneS_3)(PPh_3)][20] and 2.3456(10) Å for the dimeric analogue [RuCl([9]aneS_3)(PPh_3)]$_2$.[21] The trans-influence of the PPh_3 group also affects the distance between S(2) and the aromatic carbon atom C(3), which is slightly elongated when compared to S(1)−C(2) (1.83(1) and 1.784(11) Å, respectively). The unsymmetrical structure of **7** observed in solution is also seen in the solid state where PPh_3 eclipses one of the CH_2−CH_2 bonds (isomer **A** in Figure 3). A steric origin for this conformation is suggested by the fact that analogous complexes with more flexible macrocycle units[13] or bearing smaller auxiliary ligands in place of PPh_3[13,22] all form symmetrical structures (isomer **B**) in the solid state.

Scheme 5



Discussion

The insertion reactions of thioalkynes with the benzyne−nickel(0) complex **2** show very good regioselectivities that can be rationalized both by the polarization of the triple bond and by the coordination ability of the sulfur atom. The first insertion of MeC≡CS-p-Tol, leading to the nickelaindene **8** (Scheme 5), can be described as a reaction of the electron-rich benzyne fragment with the more electrophilic carbon atom of the triple bond, as previously proposed for analogous double insertion reactions of ester-activated alkynes.[9,10,23] The second insertion step is assumed to take place in the Ni−aryl bond due to the stabilization of the Ni−vinyl bond by partial coordination of the thioether group, as in the case of the reactions with alkynylphosphines.[11,12] The favored regiochemistry of the second insertion step, leading to the seven-membered nickelacycle **10**, is best accounted for by a coordination of the sulfur atom, where most of the electron density is located,[24] to the nickel atom during the transition state as depicted in **9**; reductive elimination of nickel(0) from **10** will yield the isolated 2,3-dithio product **4**. Other electronic factors are, however, not excluded. We have shown recently by DFT analyses of the reactions of various alkynes with phosphanickelacycles that alkyne π-orbitals can determine the regiochemistry of the insertion.[25,26] With a nickelaindene closely related to **8**, [Ni{o-C_6H_4C(CO_2Me)=C(CO_2Me)}(dcpe)], the preferred naphthalenic regioisomer (calculated or experimental) obtained from insertion of ester-substituted alkynes arises from a

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seven-membered nickelacycle analogous to **10** in which the electron-withdrawing ester group is located adjacent to nickel.[25] Although the electron densities of the alkyne carbons of the thioalkynes $MeC^{\beta}\equiv C^{\alpha}SR$ and of methyl 2-butynoate, as measured by ^{13}C NMR spectroscopy, are very similar (C^{β} is ca. 20 ppm more deshielded than C^{α}), the frontier orbitals of the thio- and ester-substituted alkynes are different due to the π-donating ability of the sulfur atom;[24] hence an alternative regiocontrol may be expected in the case of the thioalkynes for an orbital-controlled reaction. This difference between $MeC\equiv CS$-*p*-Tol and $MeC\equiv CCO_2Me$ (or $MeC\equiv CPPh_2$) most likely accounts for the formation of small amounts of the alternative 1,3-dithio regioisomer **3**, a regioisomer that is not observed in the case of the other two alkynes. Hence, the predominant factor responsible for the formation of **4** as the major product is most likely coordination of the heteroatom to the metal center during the insertion step. A similar argument has already been proposed for the very good regioselectivities observed for the insertions of propargyl alcohols into palladium−carbon bonds[27−29] or for the regiospecific insertions of alkynylphosphines with nickelacycles.[12,30]

The analogous double insertion of the diyne $(MeC\equiv CSCH_2CH_2)_2S$ to form **5** is regiospecific, and this is readily understood when looking at a molecular model of the corresponding monoinsertion nickelaindene **8** (Scheme 5). The seven-atom chain linking the vinyl moiety to the unreacted alkyne is too long to enable insertion into the Ni−vinyl bond but has exactly the required length to bring the triple bond in the coordination sphere of nickel for an insertion into the Ni−phenyl bond as depicted in **11**. The length of the chain also prevents the rotation of the alkyne, hence preventing the formation of the regioisomer having the sulfur group adjacent to the arene. Insertion will lead to **12**, from which the macrocyclic product **5** is formed by reductive elimination. With an extended chain between the two alkyne groups, e.g., by use of $(HC\equiv CCH_2SCH_2CH_2)_2S$, attempted reactions did not give any naphthalenic products.

The preparation of naphthalenes selectively substituted in the 2 and 3 positions by reactive groups for use as chelating ligands is notoriously difficult, and in this context, few preparations of such compounds bearing thiol[31,32] or thioether groups[33−35] have been reported. Some naphthalene-2,3-dithiolato complexes have been prepared with tungsten(VI) as models for oxidoreductases[32] or with gold(III) for the study of their luminescent properties,[31] but to the best of our knowledge, no coordinated thioether analogue has been reported and complex **6** represents the first example.

Macrocycles attached to a 2,3-disubstituted naphthalene or larger polyaromatic species are also quite rare. Several naphtho crown-ethers have been reported (18-crown-6, 15-crown-5, and 12-crown-4),[36] but the preparation of the nine-membered analogue naphthotrioxacyclononane, $2,3\text{-}O(C_2H_4O)_2C_{10}H_6$, has only recently been achieved in low yield.[37] A triphenylene incorporating three 9-crown-3 ether units has been obtained by trimerization of a benzo-9-crown-3 precursor,[38] while a phenanthrene analogue has been prepared by an electrochemical method,[39] but **5** is the first sulfur naphtho macrocycle to be prepared and coordinated to a transition metal. Although the methodology described here involves the use of some reactive organometallic species, it does allow the preparation of these new sulfur ligands in very good yields. The only drawback is in the purification step of **5**, during which some decomposition occurs, most likely by cleavage of a $S-CH_2$ bond. Such a fragmentation is observed in the mass spectrum of the compound, and it has been reported to occur with several related ruthenium complexes.[40,41] In our case, it is not known whether this cleavage is catalyzed by the presence of nickel salts.

The reaction of the dithioether naphthalene **4** with $[RuCl_2(PPh_3)_4]$ afforded the dinuclear complex **6** and not the expected monomer $[RuCl_2\{2,3\text{-}(TolS)_2\text{-}1,4\text{-}Me_2C_{10}H_4\text{-}\kappa S,S\}(PPh_3)_2]$ (**13**), and although some signals observed during the ^{31}P NMR monitoring of the reaction seem to indicate that **13** was formed, it reacted further to yield **6**. Ruthenium dinuclear complexes linked by three chloro bridges are quite common. Species with two unsymmetrical terminal faces have been described, but these compounds have generally been obtained with phosphines or arsines as auxiliary ligands;[14,42−45] complex **6** is the first example of such a ruthenium complex incorporating thioether ligands. These complexes, spanning the oxidation states II,II, II,III, and III,III, have been studied extensively for their spectroelectrochemical

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behaviors, as the oxidation of the Ru^{II},Ru^{II} complex to a mixed-valence species Ru^{II},Ru^{III} is usually accompanied by the generation of an intense color. These complexes have been referred to as ruthenium "blues".[15,46] Accordingly, dinuclear Ru^{II},Ru^{II} complex **6** undergoes two distinct reversible oxidations at −60 °C: the first one occurs at +0.62 V (vs Ag−AgCl) and the second one at +1.44 V. These findings closely resemble the stepwise redox behavior of the structurally related species $[(R_3P)_2(L)Ru(\mu\text{-}Cl)_3RuCl(PR_3)_2]$ (L = PR_3, CO, CS). The first oxidation, resulting in a Ru^{II},Ru^{III} mixed-valence species, is understood to be centered more on the ruthenium bearing the terminal chloride, whereas the second one is more on the $Ru(L)(PR_3)_2$ site or, presumably in the case of **6**, the ruthenium chelated by the dithioether group.[42,43,47] The $E°$ values reported for those $Ru_2Cl_4L_5$ complexes depend on the nature of the auxiliary phosphines, but are similar to those of **6**; for example, the first oxidation takes place at 0.43 V for $[(Et_2PhP)_3Ru(\mu\text{-}Cl)_3RuCl(PPhEt_2)_2]$ (**14**) (vs Ag−AgCl),[43,46] 0.71 V for $[(Ph_2MeP)_3Ru(\mu\text{-}Cl)_3RuCl(PMePh_2)_2]$,[43] 0.52 V for $[(Ph_3P)_2(CO)Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**15**),[42] and an estimated value of ca. 0.65 V for $[(Ph_3P)_3Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (**16**),[48] while the related cationic species $[(R_3P)_3Ru(\mu\text{-}Cl)_3Ru(PR_3)_3]^+$ have higher oxidation potentials, e.g., 1.28 V for $[(Ph_3P)_3Ru(\mu\text{-}Cl)_3Ru(PPh_3)_3]^+$.[42]

The value of the second oxidation and the associated difference ΔE between the first and the second oxidation step depends in part on the asymmetry of the complex. The value of ΔE (0.82 V in the case of **6**) is widely taken as a qualitative or even quantitative reflection of the bonding between the two metals, but this is only valid under restricted circumstances.[15] Complex **15** does not show a second oxidation due to the electron-withdrawing character of the CO ligand, but the pentakisphosphine analogues **14** and **16** have $Ru^{II},Ru^{III}/Ru^{III},Ru^{III}$ couples at 1.46 and 1.49 V, respectively, with corresponding ΔE values of 1.03 and 0.95 V. Hence, from these data, it is possible to conclude that the effect of the chelating aromatic thioether group on the electrode potential is close to that of two PPh_3 ligands; if anything, the thioether groups marginally facilitate oxidation.

In summary, benzyne−nickel complexes represent a useful synthetic tool for the preparation of novel thioether-based ligands having polyaromatic backbones. These thioethers have shown interesting potentials as ligands and, although this methodology does not seem to allow preparation of crown-ethers larger than cyclononanes, the luminescent properties of these compounds are being investigated for their possible use as optical molecular sensors.

Experimental Section

General Procedures. All experiments involving benzyne complexes were carried out under argon using standard Schlenk techniques, while preparations of the ruthenium complexes were carried out under nitrogen. All solvents were dried and degassed prior to use. NMR spectra were recorded on a Varian XL-200E (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz), a Varian Gemini 300BB, or a Varian Mercury 300 (^1H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121.4 MHz). The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^1H) were ^1H-decoupled. The coupling constants (J) are given in Hz with an estimated error of ±0.2 Hz. Infrared spectra were measured on a Perkin-Elmer Spectrum One instrument. Mass spectra of the complexes were obtained on a ZAB-SEQ4F spectrometer by the fast-atom bombardment (FAB) technique, and those of the organic ligands on a Fisons VG Autospec instrument by electron impact (EI). The microanalyses were done in-house.

The electrochemical measurements of **6** were recorded on a PAR 170 potentiostat controlled by ADI MacLab 400 interface and ADI Echem 5.1 software, using a jacketed 10 mL cell cooled to −60 °C and equipped with 1 mm platinum disk working, Pt auxiliary, and nonaqueous Ag−AgCl reference electrodes. Scan rates ranged from 50 to 3000 mV/s for cyclic voltammetry with routine scans at 100 mV/s. Alternative current voltametry was scanned at 20 mV/s, and the frequencies were surveyed between 40 and 1000 Hz, with 105 Hz as routine. The solutions contained 0.5 M $[N^nBu_4][PF_6]$ and 3×10^{-4} M of complex **6** in dry, degassed CH_2Cl_2. The solutions were purged and maintained under an atmosphere of nitrogen. The values are referenced to an internal ferrocene/ferrocenium couple ($E° = 0.56$ V, $\Delta E_p = 0.09$ V).

Starting Materials. The thioalkyne MeC≡CS-*p*-Tol was prepared according to a published procedure[49] by initial formation of $HC{\equiv}CCH_2S$-*p*-Tol from addition of *p*-toluenethiol to propargyl bromide, followed by isomerization of the triple bond to the internal position with anhydrous KOH. The diyne $(MeC{\equiv}CSCH_2CH_2)_2S$ was obtained similarly by reaction of $(HSCH_2CH_2)_2S$ with propargyl bromide and subsequent treatment with KOH.[50] The complexes $[RuCl_2(PPh_3)_4]$[51] and $[NiBr(C_6H_4Br\text{-}2)(PEt_3)_2]$[9] were prepared following a published procedure.

Reaction of $[Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2]$ (2) with MeC≡CS-*p*-Tol. A solution of **2** in hexane at −70 °C, freshly prepared from lithium reduction of $[NiBr(C_6H_4Br\text{-}2)(PEt_3)_2]$ (**1**) (558 mg, 1.05 mmol),[9] was treated with solid MeC≡CS-*p*-Tol (398 mg, 2.6 mmol). The solution was warmed to room temperature over 2 h and stirred for another 3 h. Monitoring of the solution by ^{31}P NMR showed complete desappearance of the signal at δ_P 27.8 due to **2**. The solvent was removed vacuo and the residue filtered through a silica gel column (hexane/ether, 4:1). Isolation was achieved by preparative TLC (hexane/toluene, 5:1) and yielded 46 mg of $1,3\text{-}(p\text{-}TolS)_2\text{-}2,4\text{-}Me_2C_{10}H_4$ (**3**) (11%) and 242 mg of $2,3\text{-}(p\text{-}TolS)_2\text{-}1,4\text{-}Me_2C_{10}H_4$ (**4**) (58%, based on **1**) as white sticky solids.

3: ^1H NMR (200 MHz, $CDCl_3$): δ 2.21 (s, 3H, CH_3^{Tol}), 2.24 (s, 3H, CH_3^{Tol}), 2.82 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 6.81 (d, 2H, $J_{HH} = 8.2$, H^{arom}), 6.82 (d, 2H, $J_{HH} = 8.2$, H^{arom}), 6.93 (d, 2H, $J_{HH} = 8.2$, H^{arom}), 6.97 (d, 2H, $J_{HH} = 8.2$, H^{arom}), 7.51−7.56 (m, 2H, $H^{6,7}$), 8.10−8.15 (m, 1H, H^8), 8.64−8.70 (m, 1H, H^5). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 18.58 (CH_3), 20.93 ($2xCH_3^{Tol}$), 22.11 (CH_3), 125.43 (CH), 125.50 (CH), 125.87 (2xCH), 125.94 (2xCH), 127.33 (CH), 127.81 (CH), 129.59 (2×CH), 129.70 (2×CH), 130.86 (C), 132.29 (C), 134.37 (C), 134.48 (2×C), 134.63 (C), 135.62 (C), 143.51 (C), 146.70 (C); one C not located. EI-MS ($C_{26}H_{24}S_2$): m/z 400 (100, M^+). HR-MS: calcd for $C_{26}H_{24}S_2$, 400.131945; found, 400.132031.

4: IR (KBr): 3064 (w), 3004 (w), 2945 (w), 2615 (m), 2855 (w), 1594 (w), 1537 (w), 1489 (vs), 1445 (m), 1085 (s), 1015 (s), 799 (vs), 755 (vs) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.23 (s, 6H, $2{\times}CH_3^{Tol}$), 2.92 (s, 6H, $2{\times}CH_3$), 6.84 (d, 4H, $J_{HH} = 8.2$, H^{arom}), 6.94 (d, 4H, $J_{HH} = 8.2$, H^{arom}), 7.56−7.64 ([AA′BB′] m, 2H, $H^{6,7}$), 8.10−8.16 ([AA′BB′] m, 2H, $H^{5,8}$). $^{13}C\{^1H\}$ NMR (75.4

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Table 3. Crystal and Structure Refinement Data for Compounds 6 and 7

	6	**7**
(a) Crystal Data		
chemical formula	$C_{80}H_{69}Cl_4P_3Ru_2S_2\cdot 3.83C_7H_8$	$C_{34}H_{33}Cl_2PRuS_3\cdot C_2H_2Cl_4$
fw	1886.60	908.63
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	16.98600(10)	13.5790(5)
b (Å)	18.24120 (10)	16.3535(7)
c (Å)	18.90320(10)	17.7432(9)
α (deg)	114.4387(3)	
β (deg)	92.4771(3)	108.750(2)
γ (deg)	114.4387(3)	
V (Å^3)	4679.86(5)	3731.0
D_c (g cm^{-3})	1.337	1.617
Z	2	4
μ (mm^{-1})	0.58 (Mo Kα)	1.088 (Mo Kα)
(b) Data Collection, Processing, and Refinement		
2θ max (deg)	60.12	46.16
data collected (h,k,l)	(−23,−25,−26) to (23,25,26)	(−14,−17,−19) to (14,18,19)
total no. of reflns	140 553	29 287
no. of unique reflns (R_{int}/%)	27 362 (4.2)	5214 (10.0)
no. of reflns obsd	18 759 [$I > 3\sigma(I)$]	2257 [$I > 3\sigma(I)$]
abs corr	integration	integration
(transmn factors)	(0.766 to 0.886)	(0.801 to 0.953)
no. of params	990	424
R	0.0356	0.0452
R_w	0.0400	0.0498

MHz, $CDCl_3$): δ 19.08 ($C^{1,4}$-CH_3), 20.97 (CH_3^{Tol}),125.64 ($C^{5,8}$-H), 126.42 (CH^{Ph}), 126.85 ($C^{6,7}$-H), 129.39 (CH^{Ph}), 133.15 (C), 134.33 (C), 134.89 (C), 135.44 (C), 139.91 (C). EI-MS ($C_{26}H_{24}S_2$): m/z 400 (100, M$^+$), 262 (45). HR-MS: calcd for $C_{26}H_{24}S_2$, 400.131945; found, 400.132310.

Reaction of [Ni(η^2-C_6H_4)(PEt_3)$_2$] (2) with (MeC≡CS-C_2H_4)$_2$S. A solution of (MeC≡CSC_2H_4)$_2$S (249 mg, 1.08 mmol) in ether (5 mL) was slowly added to a solution of **2** in hexane at −70 °C, freshly prepared from lithium reduction of [NiBr-(C_6H_4Br-2)(PEt_3)$_2$] (**1**) (575 mg, 1.08 mmol). The solution was slowly warmed to room temperature over 4 h and left stirring overnight. Monitoring of the solution by ^{31}P NMR showed the reaction to be complete. The solvent was removed in vacuo and the residue filtered through a silica gel column (ether). Separation by preparative TLC (hexane/ether, 3:2) yielded 150 mg of 2,3-S(C_2H_4S)$_2$-1,4-$Me_2C_{10}H_4$ (**5**) (45%, based on **1**) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.39−2.43 (m, 4H, CH_2), 2.81 (s, 6H, 2×CH_3), 2.86−2.89 (m, 4H, CH_2), 7.28−7.31 ([AA′BB′] m, 2H, $H^{6,7}$), 7.79−7.82 ([AA′BB′] m, 2H, $H^{5,8}$). ^{13}C-{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ 18.78 (CH_3), 34.87 (CH_2), 38.94 (CH_2), 125.79 ($C^{5,8}$-H), 126.60 ($C^{6,7}$-H), 133.26 (C), 137.82 (C), 138.01 (C). EI-MS ($C_{16}H_{18}S_3$): m/z 306 (85, M$^+$), 246 (95, M$^+$ − C_2H_4S), 231 (65), 218 (45), 71 (84), 57 (100). HR-MS: calcd for $C_{26}H_{24}S_2$, 306.057066; found, 306.057302.

Reaction of 2,3-(p-TolS)$_2$-1,4-$Me_2C_{10}H_4$ (4) with [$RuCl_2$-(PPh_3)$_4$]. A mixture of **4** (53 mg, 0.13 mmol) and [$RuCl_2$-(PPh_3)$_4$] (180 mg, 0.15 mmol) in chloroform (2 mL) was heated at 30 °C for 40 h. A solid precipitate was obtained by addition of ether, which was redissolved in toluene and crystallized by addition of a layer of hexane. Orange-red crystals of [(PPh_3)-{2,3-(MeC_6H_4S)$_2$-1,4-$Me_2C_{10}H_4$}Ru(μ-Cl_3)RuCl(PPh_3)$_2$] (**6**) (65 mg), suitable for X-ray analysis, were isolated in 57% yield (based on Ru). IR (KBr): 3047 (m), 2917 (w), 1586 (w), 1572 (w), 1481 (m), 1433 (s), 1086 (m), 802 (w), 744 (m), 696 (vs), 542 (m), 525 (vs), 516 (s), 503 (m) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.18 (s, 6H, 2×CH_3^{Tol}), 2.31 (s, 3H, CH_3), 2.34 (s, 3H, CH_3) 6.64 (d, 4H, J_{HH} = 8.0, H^{Tol}), 6.78 (d, 4H, J_{HH} = 8.0, H^{Tol}), 6.93 (t, 12H, J 7.6, PPh), 7.04−7.35 (m, 27H, PPh), 7.56−7.64 (m, 8H, $H^{6,7+PPh}$), 7.91−7.95 ([AA′BB′] m, 2H, $H^{5,8}$). ^{31}P-{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 48.2 (d, 2P, J_{PP} 1.5), 50.3 (t, 1P, J_{PP} 1.5). FAB-MS (NBA, $C_{80}H_{69}Cl_4P_3Ru_2S_2$) m/z 1532 (100, M$^+$), 1496 (M$^+$ − Cl), 1268 (M$^+$ − PPh_3), 1233 (M$^+$ − PPh_3 − Cl). Anal. Calcd for $C_{80}H_{69}Cl_4P_3Ru_2S_2$: C, 62.74; H, 4.54; P, 6.07. Found: C, 62.21; H, 4.68; P, 5.77.

Reaction of 2,3-S(C_2H_4S)$_2$-1,4-$Me_2C_{10}H_4$ (5) with [$RuCl_2$-(PPh_3)$_4$]. Solid [$RuCl_2$(PPh_3)$_4$] (224 mg, 0.18 mmol) was added at room temperature to a solution of naphthotrithiocyclononane **5** (73 mg, 0.24 mmol) in ether (5 mL). After 5 min, a beige suspension was formed, while monitoring by ^{31}P NMR spectroscopy showed the solution to contain only free PPh_3. The solvent was decanted, and the very insoluble solid was extracted with hot CH_2Cl_2 (ca. 100 mL) and filtered through Celite. Evaporation of the solvent yielded [$RuCl_2${2,3-S(C_2H_4S)$_2$-1,4-$Me_2C_{10}H_4$-$\kappa S,S,S$}(PPh_3)] (**7**) as a yellow powder (120 mg, 88% based on Ru), and single crystals suitable for X-ray analysis were obtained by diffusing ether into a solution of **7** in 1,1,2,2-tetrachloroethane. IR (KBr): 3051 (w), 2966 (w), 2927 (w), 1584 (w), 1545 (w), 1481 (m), 1434 (s), 1094 (s), 749 (s), 738 (s), 696 (vs), 510 (vs), 507 (s), 498 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63−1.80 (m, 1H, CH_2), 2.10−2.44 (m, 5H, CH_2), 2.87 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 3.20−3.30 (m, 1H, CH_2), 3.56−3.66 (m, 1H, CH_2), 7.35−7.42 (m, 8H, $H^{5,8+PPh3}$), 7.60−7.66 (m, 3H, H^{PPh3}), 7.96−8.06 (m, 7H, $H^{6or7+PPh3}$), 8.10−8.14 (m, 1H, H^{7or6}). ^{13}C{^{1}H} NMR (50.2 MHz, $C_2H_2Cl_4$+CD_2Cl_2): δ 17.54 (CH_3), 18.26 (d, J_{PC} 1.9, CH_3), 33.67 (CH_2), 37.62 (d, J_{PC} 5.9, CH_2), 37.70 (d, J_{PC} 1.2, CH_2), 42.27 (CH_2), 128.13 (d, J_{PC} 9.5, CH^{PPh3}), 128.59 (CH^{PPh3}), 129.89 (CH^{PPh3}), 132.25 (d, J_{PC} 2.4, C), 133.74 (d, J_{PC} 8.0, C^{PPh3}), 134.43 (C), 134.63 (d, J_{PC} 4, CH), 134.72 (2×CH), 134.79 (d, J_{PC} 7.8, CH), 134.75 (C), 135.46 (d, J_{PC} 5.7, C), 136.25 (C), 137.71 (d, J_{PC} 1.9, C). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 33.8. FAB-MS (NOPE, $C_{80}H_{69}Cl_4P_3Ru_2S_2$): m/z 705 (M$^+$ − Cl), 677 (M$^+$ − C_2H_4 − Cl), 486, 355. Anal. Calcd for $C_{34}H_{33}Cl_2PRuS_3\cdot 2C_2H_2Cl_4$: C, 42.40; H, 3.46. Found: C, 41.62; H, 3.74.

X-ray Crystallography of 6·3.8C_7H_8 and 7·$C_2H_2Cl_4$. Crystal data, details of data collection, data processing, structure analysis, and structure refinement are in Table 3. The crystals were mounted onto a quartz fiber and recorded at 200 K on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were measured by use of COLLECT,[52] while the intensities of the reflections were processed and the data reduced by use of the computer programs Denzo and Scalepak.[53] The structures were solved by direct methods (SIR92).[54]

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[52] *COLLECT Software*; Nonius BV, 1997−2001.

In the crystal structure of $\mathbf{6}\cdot 3.8C_7H_8$, each molecular species was accompanied by four molecules of toluene, two of which were perfectly defined, but small restraints had to be applied to the geometry of the remaining two solvate molecules. The non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were included at geometrically determined positions (C−H 1.00 Å) and periodically recalculated, but they were not refined. The maximum and minimum peaks in the final difference Fourier map were 1.59 and −1.88 e/Å^3, respectively.

The crystal of $\mathbf{7}\cdot C_2H_2Cl_4$ diffracted very weakly and the reflection/parameter ratio is lower than ideal; however all non-hydrogen atoms including those of the 1,1,2,2-tetrachloroethane solvent molecule could be refined anisotropically by full matrix least squares. Hydrogen atoms were included at calculated positions (C−H 1.00 Å) and left riding with their carbon of attachment. The methyl hydrogen atoms were orientated to best fit peaks in a difference electron density map. The maximum and minimum peaks in the final difference Fourier map were 1.71 and −0.54 e/Å^3, respectively, the biggest peaks being located close to the ruthenium atom.

The calculations were performed with use of the crystallographic software packages teXsan,[55] maXus,[56] and CRYSTALS.[57] The neutral atom scattering factors were taken from ref 58. Mass attenuation coefficients used were those implemented in maXus.[56]

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Supporting Information Available: Tables giving full crystallographic data for $\mathbf{6}\cdot 3.8C_7H_8$ and $\mathbf{7}\cdot C_2H_2Cl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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