DPPE) with ν_{CO} = 1994.9 (m) and 1906.1 (m) cm^{-1} was identical with that reported earlier.[58]

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Registry No. I·(BF_4), 15557-71-8; IIa·(PF_6), 37504-44-2; IIb·(BF_4), 96412-38-3; IIIa·(PF_6), 54039-57-5; IIIb·(PF_6), 54039-59-7; IIIc·(PF_6), 104350-97-2; IIId·(PF_6), 104350-98-3; IIIe·(PF_6), 68166-17-6; IIIf·(PF_6), 104350-99-4; IIIg·(PF_6), 54039-52-0; $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(cO)_9(PPh_3)$, 14592-26-8; $Mn_2(CO)_9P(OPh)_3$, 24476-72-0; $Mn_2(CO)_9PPh_2Me$, 61943-58-6; $Mn_2(CO)_9PEt_3$, 109335-73-1; $Mn_2(CO)_9PPhMe_2$, 50540-29-9; $Mn_2(CO)_9(\eta'$-DPPE), 109335-87-7; $Mn_2(CO)_8(PPh_3)_2$, 10170-70-4; $Mn_2(CO)_8[P(OPh)_3]_2$, 15529-62-1; $Mn_2(CO)_8(PEt_3)_2$, 15529-60-9; $Mn_2(CO)_8(PMe_2Ph)_2$, 55029-78-2; $Mn_2(CO)_8[P(p\text{-tol})_3]_2$, 63588-37-4; $Mn_2(CO)_8(PPh_2Et)_2$, 15444-76-5; $Mn_2(CO)_8(PPhEt_2)_2$, 15444-75-4; $Mn_2(CO)_8(PPh_2Me)_2$, 63393-52-2; $Mn_2(CO)_8(PPh_3)[P(OPh)_3]$, 109335-75-3; $Mn_2(CO)_8[P(OPh)_3]P(p\text{-}CH_3C_6H_4)_3$, 109335-76-4; $Mn_2(CO)_8[P(OPh)_3]PPh_2Et$, 109335-77-5; $Mn_2(CO)_8[P(OPh)_3]PPhEt_2$, 109335-78-6; $Mn_2(CO)_8[P(OPh)_3]PEt_3$, 109335-79-7; $Mn_2(CO)_8[P(OPh)_3]PPh_2Me$, 109335-80-0; $Mn_2(CO)_8[P(OPh)_3]PPhMe_2$, 109335-81-1; $Mn_2(CO)_8(PPh_3)(PPh_2Et)$, 109335-82-2; $Mn_2(CO)_8(PPh_3)(PPhEt_2)$, 109335-83-3; $Mn_2(CO)_8(PPh_3)(PEt_3)$, 109335-84-4; $Mn_2(CO)_8(PPh_3)(PPh_2Me)$, 109335-85-5; $Mn_2(CO)_8(PPh_3)(PPhMe_2)$, 109363-36-2; Mn(CO)6·, 104350-83-6; $NaMn(CO)_5$, 13859-41-1; $HMn(CO)_4PPh_3$, 16925-29-4; $HMn(CO)_4P(p\text{-tol})_3$, 104419-62-7; $HMn(CO)_4PPh_2Et$, 92816-72-3; $HMn(CO)_4PPhEt_2$, 104350-79-0; $HMn(CO)_4PEt_3$, 68199-71-3; $HMn(CO)_4PPh_2Me$, 104350-80-3; $HMn(CO)_4PPhMe_2$, 104419-63-8; $Mn(CO)_4P(OPh)_3^-Na^+$, 59778-90-4; $M(CO)_4PPh_3^-$, 53418-18-1; $Mn(CO)_4(\eta^1$-DPPE)$^-Na^+$, 109335-86-6; $Mn(CO)_4(PPh_3)$·, 14971-47-2; $HMn(CO)_3(PEt_3)_2$, 109335-74-2; $HMn(CO)_3(\eta^2$-DPPE), 36352-75-7; $Mn(CO)_3(\eta^2$-DPPE)Br, 37523-64-1; $Mn(CO)_2(\eta^2$-DPPE)$_2^+Cl^-$, 14239-02-2; Mn, 7439-96-5.

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Model Studies of Thiophene Hydrodesulfurization Using (η-Thiophene)Ru(η-C_5H_5)$^+$: Reactions Leading to C–S Bond Cleavage

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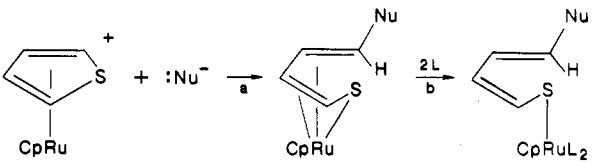
As models for the adsorption and reactions of thiophenes on hydrodesulfurization (HDS) catalysts, the thiophene π-complexes (η-thiophene)RuCp$^+$, where the thiophene is thiophene, 2-methylthiophene, or 2,5-dimethylthiophene and Cp = η-C_5H_5, have been prepared by reactions of these thiophenes with $CpRu(NCMe)_3^+$ or with $CpRu(PPh_3)_2Cl$ and $AgBF_4$. Nucleophilic (Nu = MeO^-, MeS^-, EtS^-, *i*-PrS^-, and $CH(CO_2Me)_2^-$) addition (step a) to a carbon adjacent to the S in the thiophene and 2-methylthiophene



π-ligands results in cleavage of a C–S bond to give the product with a butadienethiolate ligand coordinated through the sulfur and all four unsaturated carbon atoms. Upon reaction (step b) with phosphines (L), the two olefins are displaced leaving the butadienethiolate ligand coordinated only via the sulfur in the product $CpRu(L)_2$(*cis*,*trans*-SC(R)=CHCH=CH(Nu)). Step a provides a basis for understanding how C–S bond cleavage might occur in the catalytic HDS of thiophene on heterogeneous catalysts.

Introduction

An understanding of the catalytic hydrodesulfurization (HDS) of organosulfur compounds in petroleum is a formidable problem of continuing interest.[2] Despite decades of research primarily focused on the reactions of individual sulfur-containing compounds over industrially relevant catalysts,[3] most fundamental aspects of these important reactions have yet to be established. Several mechanistic proposals for the desulfurization of organosulfur compounds such as thiophene, benzothiophene, and dibenzothiophene have been suggested; however, there is little

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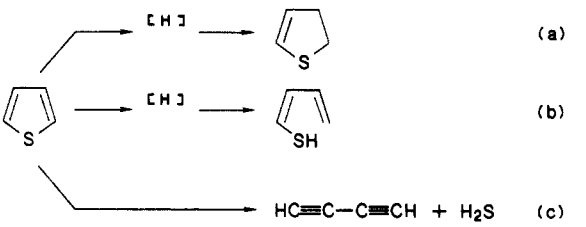
experimental evidence to support any one of them. Important mechanistic concepts for other heterogeneously catalyzed reactions have been developed by studying homogeneous organometallic model compounds.[4] This approach has only recently been applied to the study of hydrodesulfurization reactions.[5] We report herein some of our recent results that suggest a preferred adsorption mode and plausible mechanistic steps for the hydrodesulfurization (HDS) of thiophene and 2-methylthiophene.

In much of the recent literature[3,6] concerning the HDS of thiophene, end on, i.e., sulfur atom only, adsorption to a metal site on the catalyst surface is proposed or assumed; this presumably activates the heterocycle to the first steps in the HDS process and to deuterium exchange reactions of thiophenic hydrogen atoms. This proposed mode of adsorption is based largely on product distributions and reaction kinetics as well as a theoretical study of model transition-metal sulfides by SCF–Xα molecular orbital techniques.[7] Examination of reasonably well-characterized S-bound inorganic complexes of thiophene, however, show little evidence for strong sulfur-to-metal bonding, and no reactions have been reported for these S-coordinated thiophenes.[5c,8] These latter observations challenge the proposals that this type of adsorption activates thiophene to catalytic HDS reactions.

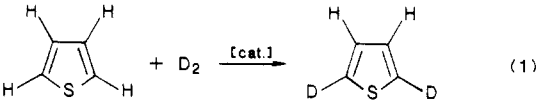
Other results are also inconsistent with the sulfur only (also called "one-point") adsorption mode. Comparisons of rates of desulfurization for thiophene, benzothiophene, and dibenzothiophene with their methyl-substituted derivatives do not show the decrease in rate expected for weaker adsorption of the methyl-substituted compounds, whose adsorption to the surface would be hindered sterically by methyl groups adjacent to the sulfur atom.[3g,h,9] Also, Zdrazil[3k] has found that the tendency of several alkyl-substituted thiophenes to adsorb on Mo-based catalytic materials is comparable with that of the corresponding benzene derivatives, supporting the proposal that they are bonding via the thiophene π-system. In addition, results of vibrational studies have been interpreted to suggest that thiophene adsorbs to Ni(111) in a planar fashion with respect to the metal surface.[10] These observations are most consistent with an adsorption mode involving the entire aromatic ring π-coordinated to surface HDS sites. An alternative involving only one carbon–carbon double bond, i.e., η^2-π-coordination, has also been suggested in the literature.[11] While there are no transition-metal compounds exhibiting this latter coordination mode, the

Scheme I



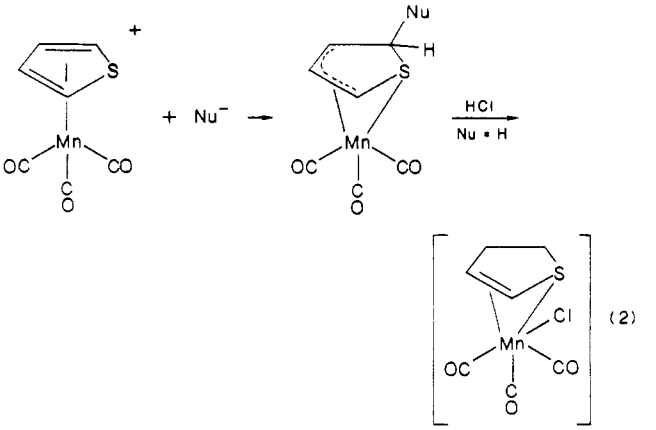
number of organometallic η^5-π-bonded complexes of thiophene has grown steadily to include $(\eta$-$C_4H_4S)Cr(CO)_3$,[12] $(\eta$-$C_4H_4S)Mn(CO)_3^+$,[5b,13] $(\eta$-$C_4H_4S)Fe(\eta$-$C_5H_5)^+$,[14a] $(\eta$-$C_4H_4S)Ru(\eta$-$C_5H_5)^+$,[5a] and $(\eta$-$C_4H_4S)M(PPh_3)_2^+$ (M = Rh, Ir).[14b] Correlations[7] between the HDS catalytic activity of metal sulfides and the electronic structure for analogous octahedral MS_6^{n-} model complexes show greatest reactivity for low-spin d^6 systems, suggesting that all of the d^6 complexes listed above may be good models for chemisorbed thiophene on HDS catalysts.

As communicated recently,[5a] the thiophene ligand in the complex $[(\eta$-$C_4H_4S)Ru(\eta$-$C_5H_5)]BF_4$ undergoes base-catalyzed H/D exchange in KOH/CD_3OD or with deuterium-enriched γ-$Al_2O_3(OH)_x$. This exchange and the exchange of thiophene with D_2 under HDS conditions[6] (eq 1) occur in both instances preferentially at the 2- and 5-positions.[15] Thus, the π-thiophene ligand serves as a realistic model for thiophene H/D exchange on HDS catalysts.[5f]



(1)

The π-thiophene ligand in $[(\eta$-$C_4H_4S)Mn(CO)_3](SO_3CF_3)$ is activated to attack by a variety of nucleophiles (eq 2)



(2)

forming nonaromatic allyl sulfide complexes, viz., $(\eta^4$-$\overline{CHCHCHCH(Nu)S})Mn(CO)_3$ (Nu = CN^-, OMe^-, $C_6H_5^-$, $SC_4H_3^-$, H^-, and $P(n$-$Bu)_3$).[5b] The hydrido adduct $(\eta^4$-$C_4H_5S)Mn(CO)_3$ subsequently reacts with HCl, protonating the ring at the 3-position, thus forming an unstable complex of 2,3-dihydrothiophene (eq 2). On the basis of these reactions, a mechanism for the initial steps in the HDS process[5b] was proposed. Prior to the above model studies of π-thiophene complexes, three types of mechanisms had

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been proposed for the HDS reaction (Scheme I): (a) direct hydrogenation of a carbon–carbon double bond to form a chemisorbed 2,3-dihydrothiophene, (b) cleavage of a carbon–sulfur bond with addition of hydrogen across this bond yielding butadienethiol, and (c) β-hydride elimination from thiophene resulting in the formation of H_2S and 1,3-butadiyne.[3,11,16] The chemistry of $(\eta\text{-}C_4H_4S)Mn(CO)_3^+$, i.e., its reactions with hydride sources and subsequent protonation, provides plausible detailed steps consistent with the first of these pathways. Interestingly, new reactivity described herein for $(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)^+$ furnishes, for the first time,[16] evidence indicating that a mechanism related to route b may also be a viable pathway in the HDS process.

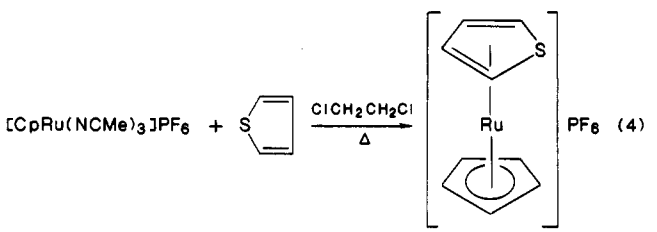
Results and Discussion

Synthesis of $(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_4H_4S)^+$. The development of new model systems for thiophene hydrodesulfurization led us to investigate the thiophene chemistry of transition metals that typically show the highest activity for the HDS reaction, e.g., Ru, Os, Rh, and Ir.[17] One of the organometallic compounds studied, $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$[18] (1), was found to react with $AgBF_4$ and thiophene in refluxing MeOH to form $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]BF_4$ (eq 3), a light brown powder, in 60% isolated

$$CpRu(PPh_3)_2Cl + AgBF_4 + C_4H_4S \xrightarrow[\Delta]{MeOH} [(\eta\text{-}C_4H_4S)RuCp]BF_4 \quad (3)$$

yield. The mechanism of η^5-thiophene formation in this reaction is not known; however, an S-coordinated intermediate, $(\eta\text{-}C_5H_5)Ru(PPh_3)_2(\eta^1\text{-}C_4H_4S)^+$, has been proposed.[5c] Reaction 3 appears not to be a simple displacement of the PPh_3 ligands since ^{31}P NMR spectra of the reaction mixtures do not show a signal corresponding to free PPh_3.

The π-thiophene complex $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]PF_6$ may also be synthesized by reaction of $[(\eta\text{-}C_5H_5)Ru(NCCH_3)_3]PF_6$[19] with thiophene in refluxing $ClCH_2CH_2Cl$ (eq 4). This preparation, used for other (arene)RuCp$^+$



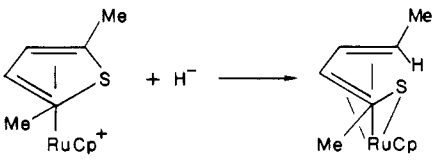
(4)

complexes,[19] is superior to that in eq 3 because the pure product is more easily isolated (79% yield) from the reaction mixture.

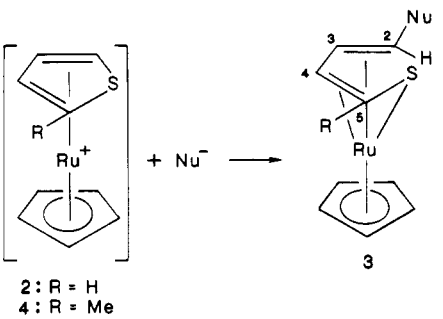
The $(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)^+$ complex is stable in the presence of air and water or when dissolved in weakly coordinating solvents such as acetone and THF. The complex does, however, undergo slow thiophene displacement at room temperature in the presence of benzene (10% displaced after 24 h in $(CD_3)_2CO$), $(n\text{-}Bu)_3P$ (85% displaced after 25 h in $(CD_3)_2CO$), CH_3CN (25% displaced after 18 h in CD_2Cl_2), and *t*-BuNC (56% displaced after 24 h in $(CD_3)_2CO$). The slow rate of thiophene displacement suggests there is strong thiophene-to-metal bonding which, in turn, activates the bound thiophene to the observed HDS-related reactivity described below and to the H/D exchange reactions reported previously.[5a,f]

Reactions of $(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)^+$ with Nucleophiles. π-Complexation of thiophene in $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]X$ (**2**: X = BF_4, PF_6) activates the heterocycle to nucleophilic attack by a variety of anions including OMe^-, SMe^-, SEt^-, $S(i\text{-}Pr)^-$, and $CH(COOMe)_2^-$.[20] The compositions of the $(\eta\text{-}C_5H_5)Ru$(thiophene·Nu) (**3**) products, which were isolated in 30–50% yield as oily solids, were established by elemental analysis and mass spectrometry. All of the adducted complexes **3** are air-stable; however, they slowly decompose both in solution and in the solid state. They are typically stored under N_2 at −20 °C.

In a related study[21] of the reactions of $(\eta\text{-}C_5H_5)Ru(\eta$-2,5-dimethylthiophene)$^+$ with hydride (H^-) donors, the structure of the $(\eta^5\text{-}C_5H_5)Ru(\eta^5$-2,5-dimethylthiophene·H) was found by X-ray crystallography to contain a butadienethiolate ligand which resulted from cleavage of a C–S bond (eq 5). In the present study, the products **3** of



(5)



(6)

reaction 6 also have the ring-opened butadienethiolate structure. This conclusion is supported primarily by ^1H and ^{13}C NMR spectra (Tables I–III) of the products. Particularly crucial to deciding whether the structure retains the C–S bond, as established for $(\eta^4\text{-}\overline{CHCHCHCH(Nu)S})Mn(CO)_3$ (eq 2),[5b] or is broken as in **3** eq (6) are the $^1J_{CH}$ coupling constants at C(2), the site of nucleophile addition. Since J_{CH} values increase with increasing s character in the C–H bond,[22] one would expect $^1J_{CH}$ to be smaller in the Mn complex where C(2) is sp^3-hybridized than in complexes of type **3** where C(2) is sp^2-hybridized. This is indeed the case as seen in the smaller $^1J_{CH}$ = 145.5 Hz value at C(2) in $(\eta^4\text{-}\overline{CHCHCHCH_2S})Mn(CO)_3$ than that (183.1 Hz) in **3** (R = H; Nu = SEt), Table II. This latter value is also much larger than $^1J_{CH}$ (144.0 Hz for equatorial H and 155.0 for axial)[23] for the sp^3 C in $\overline{SCHMeSCHMeSCHMe}$ which is bonded to two sulfur atoms as in **3** (R = H; Nu = SEt).

Also supporting different structures for the Mn and Ru complexes is their different reactivities toward the trityl cation. With $(\eta^4\text{-}\overline{CHCHCHCH_2S})Mn(CO)_3$, $Ph_3C(BF_4)$ abstracts H^- to regenerate $(\eta$-thiophene$)Mn(CO)_3^+$.[5b] It

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Table I. ^{1}H NMR and MS Data for 3, (η-C_5H_5)Ru(η^5-*cis,trans*-SCR$_{(5)}$=CH$_{(4)}$CH$_{(3)}$=CH$_{(2)}$(Nu))

		^{1}H NMR data in C_6D_6 (δ)										MS data	
R	Nu	C_5H_5	H(2)	$^3J_{2,3}$, Hz	H(3)	$^3J_{3,4}$, Hz	H(4)	$^3J_{4,5}$, Hz	H(5)	Me(5)	Nu	ion	*m/e*
H	OMe	4.55 s	5.58 d	6.6	4.84 dd	6.6	5.29 dd	4.6	6.03		3.17 s	P[e]	282
												P - *O* - Me	251
H	SEt	4.55 s	4.04 d	8.3	4.84 dd	6.4	5.35 dd	4.9	6.15 d		2.42 m[a]	P	312
											1.12 t[b]	P - SEt	251
H	SMe	4.54 s	4.08 d	8.3	4.81 dd	6.3	5.34 dd	5.4	6.13 d		1.98 s	P	298
												P - SMe	251
H	S(*i*-Pr)	4.57 s	4.02 d	8.3	4.84 dd	6.8	5.38 dd	5.2	6.17 d		2.79[c]	P	326
											1.182 d[a]	P - S(*i*-Pr)	251
											1.179 d[a]		
H	$CH(COOMe)_2$	4.51 s	3.67 dd[d]	8.6	4.58 dd	6.2	5.38 dd	5.0	6.16 d		3.29 d[d]	P	382
											3.26 s[a]	P - $CH(COOMe)_2$	351
											3.40 s[a]		
Me	OMe	4.51 s	5.64 d	6.4	4.85 dd	6.7	5.30 d			2.25 s	3.18 s	P	296
												P - OMe	265
Me	SEt	4.50 s	4.14 d	8.3	4.88 dd	6.4	5.38 d			2.19 s	2.43 m[a]	P	326
											1.14 t	P - SEt	265

[a] Diastereotopic signals due to chiral carbon atom. [b] $^3J_{H,H}$ = 7.35 Hz. [c] Septet, $^3J_{H,H}$ = 6.7 Hz. [d] $^3J_{H,H}$ = 10.1 Hz. [e] P = parent ion.

Table II. ^{13}C NMR Data in C_6D_6 (δ) for 3, (η-C_5H_5)Ru(η^5-*cis,trans*-SCR$_{(5)}$=CH$_{(4)}$CH$_{(3)}$=CH$_{(2)}$(Nu)), and 8, (η-C_5H_5)Ru(PPh_2Me)$_2$(*cis,trans*-SCR$_{(5)}$=CH$_{(4)}$CH$_{(3)}$=CH$_{(2)}$(Nu))

For Type 3 Complexes[e]

R	Nu	C_5H_5	C(2)	C(3)	C(4)	C(5)	Me(5)	Nu
H	OMe	78.0	76.2	88.7	109.1	90.5		59.4
H	SEt[a]	80.2	64.0 (183.1)	88.2 (163.5)	93.2 (162.7)	93.9 (178.1)		31.0, 14.9
Me	OMe	78.6	75.0	88.3	108.3	108.0	31.8	59.4
Me	SEt	80.2	62.6 (183.5)	87.1 (163.8)	92.6 (159.5)	111.4	32.4	31.0, 14.9

For Type 8 Complexes

R	Nu	C_5H_5	$C_{(5)}$	$C_{(2-4)}$			$R_{(5)}$	Nu	L
H	OMe	82.7	139.3[b]	105.6	122.4	149.4[c]		56.3	15.7 m, Me [144.1 m, 140.2 m, 133.7 m, 132.1 m, 128.4 m, 128.0 m, Ph]
Me	OMe	82.0	143.1[b]	108.9	125.0	143.1[c]	31.3	56.3	16.2 m, Me [144.1 m, 140.4 m, 134.0 m, 132.2 m, 128.4 m, 127.9 m, Ph]
H	SEt	82.9	145.2[b]	121.7	125.8	130.1		27.7, 15.3	16.2 m, Me [144.1 m, 140.4 m, 133.9 m, 132.3 m, 128.7 m, 128.3 m, Ph]
Me	SEt	82.1	149.3[b]	132.9	d	121.0	31.5	27.5, 15.5	16.3 m, Me [144.0 m, 140.3 m, 134.1 m, 132.2 m, 128.6 m, 128.1 m, Ph]

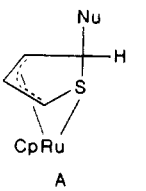
[a] Assignments confirmed by a 2D ^{13}C–^{1}H shift correlation NMR experiment. [b] Unresolved coupling to phosphorus observed. [c] Assigned to C(2). [d] Obscured by resonances of PPh_2Me. [e] $^1J_{CH}$ in Hz are given in parentheses.

also abstracts H^- and mercaptides (RS^-) from other organometallic ligands.[24,25] However, (η-2-MeC_4H_3S)Ru(η-C_5H_5)$^+$ (**4**) is not regenerated when $Ph_3C(BF_4)$ reacts with **3** (R = Me; Nu = SEt); the products of this reaction have not been identified.

The 2-methylthiophene complex [(η-2-MeC_4H_3S)Ru(η-C_5H_5)]X (**4**: X = BF_4, PF_6) also reacts with OMe^- and SEt^- to yield the complexes (η-C_5H_5)Ru(η^5-SC(R)CHCHCH(Nu)) (**3**: R = Me; Nu = OMe, SEt) as yellow powders (eq 6). Regiospecific nucleophilic attack at the non-methylated position adjacent to sulfur is supported by ^{1}H and ^{13}C NMR spectra (Tables I and II) of the products. Comparison of the thiophenic resonances in the ^{1}H NMR spectra of the methylated and non-methylated ethyl mercapto adducts (**3** (R = Me; Nu = SEt), δ 5.38 d, 4.88 dd, 4.14 d; **3** (R = H, Nu = SEt), δ 6.15 d, 5.35 dd, 4.84 dd, 4.04 d) shows that the two complexes are very similar except for the additional signal at δ 6.15 for the H at C(5) for the non-methylated complex. Similar results were obtained for the methoxy complexes.

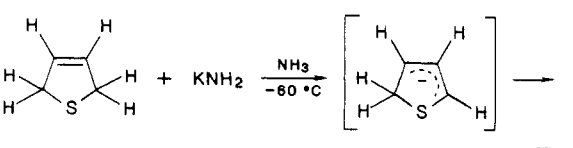
The stereochemistry at the olefinic C(2) is shown in eq 6 with the nucleophile (Nu) exo to the butadiene fragment. The primary support for this stereochemistry is the structure of the products obtained when the olefin is displaced from the metal (see below); in these, H(2) and H(3) are clearly trans to each other as indicated by the large $^3J_{HH}$ coupling constants between H(2) and H(3). These same coupling constants in complexes **3** range from 6.4 to 8.6 Hz and are consistent with the trans stereochemistry of H(2) and H(3).

In considering the details of reaction 6, it is possible that initial nucleophilic attack on **2** or **4** gives the allyl sulfide intermediate A, which undergoes C–S bond cleavage to



A

yield the butadienethiolate product **3**. That this is reasonable is suggested by the formation of butadiene thiolates from allyl sulfide intermediates in organic reactions. 2,5-Dihydrothiophene reacts with KNH_2 in liquid NH_3 at –60 °C to form *cis*-CH_2=CHCH=CHS$^-$ within 10 min (eq 7); the allyl sulfide anion $\overbrace{SCHCHCHCH_2}^{-}$ has been pos-



(7)

tulated as the reactive intermediate.[26] Diethylamine reacts

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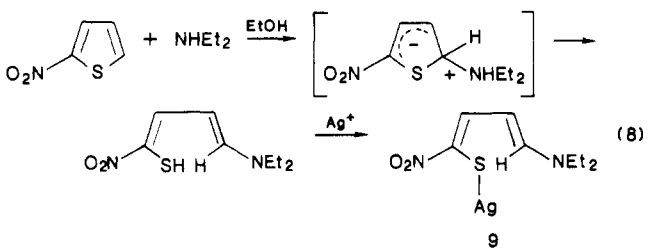
(25) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489.

Table III. ^{1}H NMR and MS Data for (η-C_5H_5)RuL_2(*cis,trans*-$SCR_{(5)}$=$CH_{(4)}CH_{(3)}$=$CH_{(2)}$(Nu)): 7 (L_2 = dppe) and 8 (L = PPh_2Me)

		^{1}H NMR data (δ)										MS data	
R	Nu	C_5H_5	R(5)	$^3J_{54}$, Hz	H(4)	$^3J_{43}$, Hz	H(3)	$^3J_{32}$, Hz	H(2)	Nu	L	ion	*m/e*
						Type 7 Complexes							
H	OMe	4.69 s[a]	4.93 d	9	5.35 dd	10	6.19 dd	13	6.43 d	3.43 s	2.8 m 2.3 m 7.2–7.9 m	P[i]	680
Me	OMe	4.68 s[b]	*c*		5.56 d	10	6.15 dd	14	6.44 d	3.49 s	2.8 m 2.2 m 7.2–7.9 m	P	694
H	SEt	4.68 s[b]	5.08 d	10	5.30 dd	10	6.71 dd	17	5.77 d	2.57 q[d] 1.22 t	2.7 m 2.2 m 7.2–7.9 m	P	710
Me	SEt	4.68[e]	*c*		5.70 d	10	6.71 dd	15	5.82 d	2.63 q[f] 1.27 t	2.8 m 2.2 m 7.1–7.8 m	P	724
						Type 8 Complexes							
H	OMe	4.43 s[b]	6.19 d	9.3	5.97 dd	9.8	6.49 dd	12.7	6.66 d	3.53 s	1.51 m 7.1–7.9 m	P – PPh_2Me P – $2PPh_2Me$ $CpRu(PPh_2Me)$ – H $CpRu(PPh_2Me)$(OMe)	482 282 366 398
Me	OMe	4.48 s[b]	1.95 s		6.14 d	10.2	6.40 dd	12.8	6.60 dd	3.42 s	1.54 m 7.1–7.9 m	P – $2PPh_2Me$ $CpRu(PPh_2Me)$ – H $CpRu(PPh_2Me)$(OMe)	296 366 398
H	SEt	4.44 s[b]	6.50 d	9.2	6.10 dd	9.7	7.20 dd	15.1	6.12 d	2.67 q[g] 1.25 t	1.51 m 7.1–7.9 m	P – PPh_2Me P – $2PPh_2Me$ $CpRu(PPh_2Me)$ – H $CpRu(PPh_2Me)$(SEt)	512 312 366 428
Me	SEt	4.47 s[b]	1.97 s		6.33 d	10.5	7.13 dd	15.1	6.02	2.57 q[h] 1.20 t	1.52 m 7.1–7.9 m	P – PPh_2Me P – $2PPh_2Me$ $CpRu(PPh_2Me)$ – H $CpRu(PPh_2Me)$(SEt)	526 326 366 428

[a] In $(CD_3)_2CO/C_6D_6$, 80:20 (v/v). [b] In $(CD_3)_2CO$. [c] Obscured by resonances of dppe. [d] $^3J_{H,H}$ = 7.2 Hz. [e] In CD_2Cl_2. [f] $^3J_{H,H}$ = 7.3 Hz. [g] $^3J_{H,H}$ = 7.35 Hz. [h] $^3J_{H,H}$ = 7.36 Hz. [i] P = parent ion.

readily with 2-nitrothiophene in ethanol in the presence of $AgNO_3$ yielding silver (*cis,trans*-4-(diethylamino)-1-nitro-1,3-butadiene-1-thiolate) (**9**).[27] As shown in eq 8,



(8)

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this reaction is postulated to occur via initial nucleophilic attack at the 5-position of the thiophene ring, followed by a ring-opening step to the butadienethiol which is subsequently trapped by Ag^+; air oxidation to the disulfide occurs in the absence of Ag^+. Interestingly, only the cis, trans isomer **9** is observed in these reactions; as noted above, the butadienethiolate ligand appears to have the same stereochemistry in the **3** products.

Not all of the attempted nucleophilic reactions were successful. Treating **2** with $(NEt_4)_2MoS_4$[28a] or $\{Cp'MoS\}_2S_2CH_2$[28b] (Cp' = C_5H_4Me) resulted in rapid thiophene displacement. As noted above, $(n\text{-Bu})_3P$ also displaces the thiophene heterocycle; ^{1}H NMR spectra gave no evidence for adduct formation, i.e., (η^4-$\overline{CHCHCHCH(P(Bu)_3)S}$)$Ru(\eta\text{-}C_5H_5)^+$. No tractable products were obtained on reaction of nucleophiles such as LiMe or LiPh with **2** or **4**. Under the conditions used to synthesize **3**, the reaction of the 2,5-dimethylthiophene complex $[(\eta\text{-}2,5\text{-}Me_2C_4H_2S)Ru(\eta\text{-}C_5H_5)]X$ (**5**: X = PF_6) with SEt^- resulted only in decomposition. Apparently, methyl groups in **4** and **5** deactivate thiophenes to nucleophilic attack at the methylated carbons, as was also observed in the (η-methylthiophenes)$Mn(CO)_3^+$ complexes.[29] Studies of nucleophilic reactions of several methyl-substituted cycloheptatrienyl complexes indicated that methyl substituents had a significant steric influence on reactivity while electronic factors were small.[30]

Reactions of the (η-C_5H_5)$Ru(\eta^5$-SC(R)CHCHCH(Nu)) (3). In contrast to the reactivity (eq 2) of (η^4-$\overline{CHCHCHCH_2S}$)$Mn(CO)_3$ (**6**: Nu = H),[5b] acids do not react cleanly with (η-C_5H_5)$Ru(\eta^5$-SC(R)CHCHCH(Nu)) (**3**: R = H, Me; Nu = OMe, SEt). Many products, as yet unidentified, were observed (by ^{1}H NMR) on reaction of **3** (R = H, Me; Nu = OMe, SEt) with MeI and $(Me_3O)PF_6$. However, reactions of **3** (R = H, Me; Nu = OMe, SEt) with excess $Ph_2PCH_2CH_2PPh_2$ (dppe) in benzene at room temperature for 1 week result in the formation of new compounds which were too unstable to be purified by column chromatography. Nevertheless, the ^{1}H NMR and mass spectrometric data (Table III) for the products support their formulation as sulfur-coordinated butadienethiolate compounds, viz., (η-C_5H_5)Ru(dppe)(*cis,trans*-$SCR_{(5)}$=$CH_{(4)}CH_{(3)}$=$CH_{(2)}$(Nu)) (**7**: R = H, Me; Nu = OMe, SEt) as shown in eq 9. The product **7** (R = H; Nu = SEt) from

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(27) Guanti, G.; Dell'Erba, C.; Leandri, G.; Thea, S. *J. Chem. Soc., Perkin Trans. 1* 1974, 2357.
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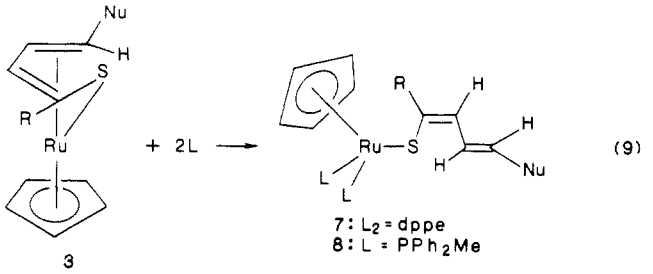


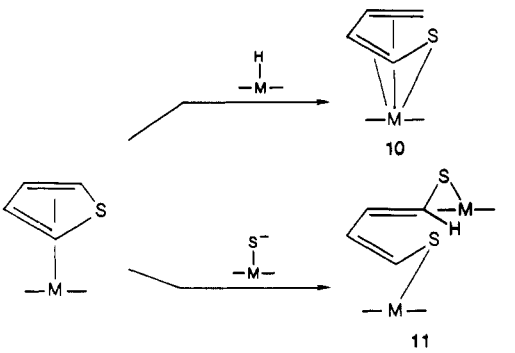
the ethyl mercapto complex of thiophene, for instance, exhibits four resonances which have been assigned to the butadiene moiety: a doublet at 5.08 ppm (H(5)), two doublets-of-doublets at 5.30 and 6.71 ppm (H(4) and H(3)), and a doublet at 5.77 ppm (H(2)). A 2D homonuclear J-correlated ^{1}H NMR study of this adduct confirms the butadiene connectivity and the assignments of the chemical shifts. The respective coupling constants ($^3J_{HH}$) of approximately 10, 10, and 17 Hz are indicative of the cis,trans stereoisomer as the only product formed.[22] The related organic compound *cis,trans*-$CH_{(5)}(CO_2Me)$=$CH_{(4)}CH_{(3)}$=$CH_{(2)}(CO_2Me)$ exhibits similar coupling constants (Hz): $^3J_{54}$ = 10.7, $^3J_{43}$ = 10.7, $^3J_{32}$ = 14.8;[31] the chemical shifts also have a similar trend (5.8 ppm, H(5); 6.5 ppm, H(4); 8.2 ppm, H(3); 5.9 ppm, H(2)) with H(3) resonating the farthest downfield. In **7** (R = H; Nu = SEt), no coupling to phosphorus is observed.

Other phosphines, such as PMe_3 and PPh_2Me, react with **3** (R = H, Me; Nu = OMe, SEt) yielding the analogous S-coordinated butadienethiolate products; the complexes incorporating PPh_2Me, **8** ($(\eta$-$C_5H_5)Ru(PPh_2Me)_2$(*cis,trans*-SCR=CHCH=CH(Nu)): R = H, Me; Nu = OMe, SEt), have been characterized by ^{1}H NMR and ^{13}C NMR spectroscopy as well as mass spectrometry (Tables II and III). The ^{13}C NMR resonances for **8** (R = H; Nu = SEt) in the butadiene region (121.7, 125.8, 130.1, 145.2 ppm) are similar to those found for *cis,trans*-MeSCH=CHCH=CHSMe (120.2, 123.9, 125.0, 128.9 ppm; $CDCl_3$).[32] All of the products **8** described above could not be isolated pure due to the fact that all attempts to isolate them from the excess ligand, L, by chromatography led to complete decomposition. Qualitatively, the rate of reaction of **3** (R = H, Me; Nu = SEt) with PPh_2Me (yielding **8**) is independent of the phosphine concentration. No reaction occurred over a 24-h period on dissolving **3** (R = H; Nu = OMe) in CD_3CN or pyridine-d_5.

Implications for the Mechanism of Thiophene Hydrodesulfurization. The thiophene rings in both (η-$C_4H_4S)Mn(CO)_3^+$ and (η-$C_4H_4S)Ru(\eta$-$C_5H_5)^+$ are susceptible to attack at the 2-position by nucleophiles. These reactions of π-bonded thiophene may serve as simple models for reactions of hydride and sulfide groups likely to be present on HDS catalyst surfaces.[33] This nucleophilic step is particularly important because it disrupts the aromatic stabilization of the thiophene ring, which is presumably the reason why it is one of the least active organosulfur compounds treated in the HDS process. Moreover, we have now demonstrated in this paper that nucleophilic addition to (η-thiophene)$Ru(\eta$-$C_5H_5)^+$ leads directly to C–S bond cleavage yielding the butadienethiolate ligand (eq 6).

On an HDS heterogeneous catalyst, initial steps in the reaction of thiophene may be viewed (Scheme II) as involving initial attack on a π-adsorbed thiophene by either a surface hydride or sulfide to give the butadienethiolate.

Scheme II



Like other mercaptans, the butadienethiolate should undergo desulfurization under HDS conditions much more readily than does thiophene.[34] Thus, sulfur removal from intermediates **10** and **11** should be fast relative to the rate of their formation. The mechanism of butadienethiolate desulfurization is not clear, but recent studies of Rakowski DuBois and co-workers[35] show that vinylthiolate complexes of Mo react with H_2 to cleave thhe C–S bond and give the hydrocarbon; such a route could be involved in cleaving the C–S bonds in the butadienethiolate in Scheme II.

Perhaps of particular significance to the HDS mechanism is the fact that nucleophilic addition to thiophene in (η-thiophene)$Mn(CO)_3^+$ leads to products in which no C–S bonds are broken, but products of the addition to (η-thiophene)$Ru(\eta$-$C_5H_5)^+$ have a cleaved C–S bond. This difference in reactivity may account for the much higher HDS activity[36] of Ru as compared with Mn.

Experimental Section

General Information. Reactions and reaction workups were performed in air unless otherwise noted. Reagents were used as received; they include $AgNO_3$ (Fisher), $AgBF_4$ (Aldrich), basic Al_2O_3 (Baker), $Ph_2PCH_2CH_2PPh_2$ (dppe), and PPh_2Me (Strem). All solvents (reagent grade) were used as received except for MeOH, which, when required dry, was distilled from NaOMe, hexanes, which was distilled from CaH_2, and THF, which was distilled from Na/benzophenone.

NaOMe was prepared from Na and dry MeOH under N_2 and was used in situ; NaSMe, NaS(*i*-Pr), NaSEt, and $NaCH(COOMe)_2$ were prepared from NaH (50% in oil, Alfa) and HSMe, HS(*i*-Pr), HSEt, or $CH_2(COOMe)_2$ (Aldrich) as follows: twice the desired quantity of NaH was washed three times with 20 mL of dry hexanes under N_2. Then, the powder, slurried in 25 mL of dry THF, was treated with excess mercaptan/malonate under N_2. After the mixture was stirred for 2 h, the volatiles were removed in vacuo; these salts were used immediately in the reactions described below, except for NaSEt which was filtered, washed with Et_2O, and isolated as a white powder. (η-$C_5H_5)Ru(PPh_3)_2Cl$[18] and [(η-$C_5H_5)Ru(\eta$-$C_6H_6)]PF_6$[19] were synthesized by reported procedures.

^{1}H and ^{13}C NMR data were obtained on a Nicolet NT-300 spectrometer; the 2D homonuclear *J*-correlated spectra of **7** (R = H; Nu = SEt) were recorded by using COSY4,[37] and the ^{13}C NMR shift assignments for **3** (R = H; Nu = SEt) were made by using the 2D X–H shift correlation program CSCM.[38] Mass spectrometry data (electron-impact MS) were collected on a Finnigan 4000 spectrometer; fast atom bombardment MS data were collected on a Kratos MS-50 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Purification of Thiophene. In a well-vented hood, 20 g of powdered $AgNO_3$ was placed in a loosely capped bottle containing

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250 g of crude thiophene (Alfa, 99%). After 7 days the yellow solution was decanted from the solid residue. To the solution was added ~5 g of CaH_2 and ~3 g of charcoal. After the mixture was refluxed for 24 h, the purified thiophene was collected by distillation at ambient pressure.

[(η-C_4H_4S)Ru(η-C_5H_5)]BF_4 (2: X = BF_4). Method I. The complex (η-C_5H_5)Ru(PPh_3)$_2$Cl (1; 1.00 g, 1.38 mmol), $AgBF_4$ (0.290 g, 1.52 mmol), and thiophene (20 mL) were refluxed in 10 mL of MeOH for 72 h under N_2. Isolation of the product was accomplished by removing the volatiles from the reaction mixture in vacuo, extracting the residue with CH_2Cl_2, and precipitating the product from the filtered solution by slow addition of Et_2O. Successive recrystallizations from CH_2Cl_2/Et_2O yielded **2** (X = BF_4) as a pale brown powder in 60% yield. ^1H NMR (acetone-d_6): δ 5.49 (5 H, s, C_5H_5), 6.50 (2 H, m, thiophene H(2,5)), 6.57 (2 H, m, thiophene H(3,4)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 81.33 (C_5H_5), 86.35, 79.10 (η-thiophene). MS (FAB, glycerol): *m/e* 251 (parent ion), 167 ((η-C_5H_5)Ru$^+$), 102 (Ru$^+$). Anal. Calcd for $C_9H_9BF_4RuS$: C, 32.07; H, 2.69; S, 9.51. Found: C, 32.12; H, 2.85; S, 9.42.

[(η-C_4H_4S)Ru(η-C_5H_5)]PF_6 (2: X = PF_6). Method II. As described by Mann et al.,[19] 0.552 g of [(η-C_5H_5)Ru(η-C_6H_6)]PF_6 (1.42 mmol) was photolyzed in CH_3CN to give [(η-C_5H_5)Ru-($NCCH_3$)$_3$]PF_6. After evaporation to dryness under vacuum, the oily solid residue was dissolved in $ClCH_2CH_2Cl$ (25 mL) containing 5 mL of thiophene. After the solution was refluxed for 16 h under N_2, the volatiles were removed in vacuo, and the residue was extracted with warm acetone. After the insoluble material was filtered off, the product (**2**: X = PF_6) was precipitated with Et_2O yielding a pale brown solid (79%, based on [(η-C_5H_5)Ru(η-C_6H_6)]PF_6). ^1H NMR (acetone-d_6): identical to **2** (X = BF_4) above. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 81.10 (C_5H_5), 87.05, 86.90 (η-thiophene).

The methylated derivatives [(η-2-MeC_4H_3S)Ru(η-C_5H_5)]X (**4**) and [(η-2,5-$Me_2C_4H_2S$)Ru(η-C_5H_5)]X (**5**) can be prepared in syntheses analogous to methods I and II. Explicit procedures have been reported with kinetic studies of the H/D exchange of these organometallic derivatives.[5f]

(η-C_5H_5)Ru(η^5-SCH=CHCH=CH(Nu)) (3: R = H; Nu = OMe, SMe, S(*i*-Pr), CH(COOMe)$_2$). In a 100-mL round-bottom flask equipped with a gas inlet, 0.100 mmol of **2** (X = BF_4 or PF_6) was added, with stirring, to a freshly prepared mixture of NaOMe/dry MeOH (2 mL), NaSMe, NaS(*i*-Pr), or NaCH-(COOMe)$_2$ (10 equiv) in dry THF (25 mL) under N_2. After 2 h at room temperature, the volatiles were removed in vacuo, and the residue was extracted with benzene (10 × 2 mL). The extracts were combined and passsed over basic Al_2O_3 (5 × 80 mm), eluting with benzene. The yellow solution was collected and pumped to dryness. This material was dissolved in a minimal amount of benzene and chromatographed over basic Al_2O_3 (5 × 80 mm) with benzene as the eluant. The yellow band was collected and pumped to dryness yielding an oily solid; yields 30–50%. Anal. Calcd for $C_{10}H_{12}ORuS$ (**3**: R = H; Nu = OMe): C, 42.69; H, 4.30. Found: C, 42.71; H, 4.21. ^1H NMR and MS data for all the compounds are reported in Table I. ^{13}C NMR data are given in Table II.

(η-C_5H_5)Ru(η^5-SCMe=CHCH=CH(OMe)) (3: R = Me; Nu = OMe). In a 100-mL round-bottom flask equipped with a gas inlet, 2 mL of dry MeOH was treated with 23 mg (1.00 mmol) of Na under N_2. After all of the Na had reacted, 25 mL of dry THF was added and then 0.100 mmol of **4** (X = BF_4 or PF_6). After being stirred for 2 h at room temperature, the reaction mixture was worked up as described above. On pumping the benzene solution to dryness, the product formed a yellow solid (observed by ^1H NMR to be solvated with some benzene) which was isolated in 40% yield; mp 35 °C. Anal. Calcd for $C_{11}H_{14}ORuS\cdot 0.7C_6H_6$: C, 45.59; H, 4.83; S, 10.66. Found: C, 45.65; H, 4.86; S, 10.94.

(η-C_5H_5)Ru(η^5-SCR=CHCH=CH(SEt)) (3: R = H, Me; Nu = SEt). In a 100-mL round-bottom flask equipped with a gas inlet, 0.100 mmol of either **2** or **4** (X = BF_4 or PF_6) and 84 mg (1.00 mmol) of NaSEt were stirred in CH_2Cl_2 (20 mL) and HSEt (1 mL) for 2 h under N_2. The volatiles were then removed in vacuo, and the reaction mixture was worked up as described two paragraphs above. **3** (R = H; Nu = SEt; yellow-orange oil; yield 60%) was characterized by its NMR and mass spectra. **3** (R = Me; Nu = SEt): yellow powder (observed by ^1H NMR to be solvated with a small amount of benzene); yield 65%; mp 52 °C. Anal. Calcd for $C_{12}H_{16}RuS_2\cdot 0.15C_6H_6$: C, 45.95; H, 5.05; S, 19.02. Found: C, 46.26; H, 5.38; S, 19.43.

Reactions of 3 (R = H, Me; Nu = OMe, SEt) with dppe. In a 100-mL round-bottom flask, 10–20 mg of **3** and 100 mg (0.251 mmol, ca. 5 equiv) of dppe were dissolved in 30 mL of benzene, sealed, and allowed to stand at room temperature for 1 week. Then the volatiles were removed in vacuo. The residue was extracted with Et_2O (15 mL) and filtered to separate the product (in the Et_2O) from excess dppe. This extraction was repeated three times. After the Et_2O was removed in vacuo, the unstable ring-opened products **7** (containing some free dppe) were characterized by ^1H NMR and mass spectrometry (Table III).

Reactions of 3 (R = H, Me; Nu = OMe, SEt) with PPh_2Me. In capped 5-mm NMR tubes was placed 10–20 mg of **3** dissolved in acetone-d_6. To each solution was added approximately 2.6 equiv of PPh_2Me. These mixtures were allowed to stand at room temperature for several days (ca. 8 for Nu = OMe, ca. 12 for Nu = SEt), until greater than 85% of the ring-opened products **8** had formed (by ^1H NMR); a small amount of decomposition was also observed. ^1H NMR and ^{13}C NMR spectra were then recorded. Mass spectrometry samples were prepared by removing the volatiles in vacuo; the reaction products obtained were oily solids containing excess PPh_2Me. They were characterized by their ^1H and ^{13}C NMR and mass spectra (Tables II and III).

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