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Utilization of CS_2 as a Source of C_1 Synthetic Units for the Preparation of Bis(alkylthio)methanes and Alkyl Dithioformates

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Double insertion of CS_2 into two Ru–H bonds of $[(dppm)_2Ru(H)_2]$ (dppm = $Ph_2PCH_2PPh_2$) affords the methanedithiolate complex $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$. The methanedithiolate moiety has been functionalized using 2 equiv of RX resulting in bis(alkylthio)methane derivatives $[(dppm)_2Ru(RSCH_2SR)][X]_2$. The bis(alkylthio)methane complex loses the bis(alkylthio)methane moiety under very mild conditions and in turn affords the $[(dppm)_2RuX_2]$ complex from which the starting dihydride $[(dppm)_2Ru(H)_2]$ has been regenerated via reaction with KOH/EtOH. On the other hand, insertion of CS_2 into one Ru–H bond of $[(dppe)_2Ru(H)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) followed by functionalization using RX results in alkyl dithioformate complex *trans*-$[(dppe)_2Ru(H)(SC(SR)H)][X]$. In this case also, the alkyl dithioformate moiety gets eliminated under very mild conditions to afford the $[(dppe)_2Ru(H)(X)]$ derivative from which the starting dihydride has been regenerated via reaction with $NaBH_4$. The reactions presented here constitute utilization of CS_2 as a C_1 synthetic source for the generation of useful organic compounds.

Introduction

The insertion of heterocumulenes such as CO_2, CS_2, and COS into metal−hydride and metal−carbon bonds of transition metal fragments is an important chemical reaction in functionalizing these species. This area of research has been receiving enormous interest due primarily to their potential as C_1 building blocks for the generation of useful organic compounds.[1]

Recently, we reported our preliminary findings on the insertion reactions of CO_2 and CS_2 into Ru−H bonds of $[(diphosphine)_2Ru(H)_2]$ (diphosphine = $Ph_2PCH_2PPh_2$ dppm, $Ph_2PCH_2CH_2PPh_2$ dppe).[2] We also communicated in another preliminary report the functionalization of the inserted CS_2 and its subsequent elimination as methyldithioformate from the metal complex.[3] In this paper, we present the complete studies of the functionalization of CS_2 and the subsequent elimination of the organic fragment from certain ruthenium complexes and demonstrate the utilization of CS_2 as a C_1 building block for the generation of bis(alkylthio)methanes and alkyl dithioformates.

Experimental Section

General Procedures. All reactions were carried out under N_2 at room temperature using standard Schlenk[4] and inert-atmosphere techniques unless otherwise specified. The ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectral data were obtained using Avance Bruker 400 and 500 MHz instruments. The shift of the residual protons of the deuterated solvent was used as an internal reference. The ^{19}F NMR spectra were recorded relative to $CFCl_3$ and the ^{31}P NMR spectra with respect to 85% H_3PO_4 as external standards. Elemental analyses were carried out at the RSIC, CDRI, Lucknow, India. Bis(diphenylphosphino)methane (dppm),[5] bis(diphenylphosphino)ethane (dppe),[6] ROTf, $TfO(CH_2)_nOTf$ (n = 2−4),[7] *cis*-/*trans*-$[(dppm)_2Ru(H)_2]$,[8] *cis*-$[(dppe)_2Ru(H)_2]$,[9] $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$,[2]

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Table 1. Numbering Scheme for the Compounds

L	compd no.	compd no. for $[(dppm)_2M(\eta^2\text{-L})][X]_2$	compd no. for $[(dppe)_2M(\eta^2\text{-L})][X]$
$MeSCH_2SMe$	**L-1**	**1**[a]	
$(PhCH_2S)_2CH_2$	**L-2**		
$(H_2C{=}CHCH_2S)_2CH_2$	**L-3**		
c-$SCH_2S(CH_2)_2$	**L-4**	**4**[a]	
c-$SCH_2S(CH_2)_3$	**L-5**	**5a**[a] **5b**[b]	
SC(SH)H	**L-6**		**6**[c]
$SC(SH_2CCH{=}CH_2)H$	**L-7**		**7**[d]
$SC(SH_2CC_6H_5)H$	**L-8**		**8**[d]
$SC(S(CH_2)_3OTf)H$	**L-9**		**9**[a]
$SC(S(CH_2)_4OTf)H$	**L-10**		**10**[a]

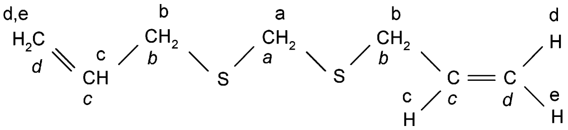
[a] X = OTf. [b] X = Br. [c] X = BF_4. [d] X = BPh_4.

and *trans*-$[(dppe)_2Ru(H)(SC(S)H)]$[3] were prepared by literature methods. The numbering scheme for the compounds reported in this work is summarized in Table 1.

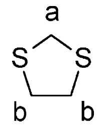
Preparation of Bis(methylthio)methane (L-1). To a $CDCl_3$ solution (0.6 mL) of $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ (0.010 g, 0.010 mmol) in a 5 mm NMR tube was added MeI (3 equiv, 4.8 μL, 0.030 mmol), and the mixture was shaken well. The color of the solution changed from reddish brown to greenish-yellow within a few minutes. After 1 day, a very clear greenish-yellow solution was obtained that was identified as a mixture of *cis*-$[(dppm)_2RuI_2]$ and bis(methylthio)methane ($MeSCH_2SMe$) (**L-1**) in quantitative yields. ^1H NMR ($CDCl_3$) spectral data for *cis*-$[(dppm)_2RuI_2]$: δ 4.94 (m, 2H, $Ph_2PCH_2PPh_2$), 5.27 (m, 2H, $Ph_2PCH_2PPh_2$), 6.49−8.25 (m, 40H, $Ph_2PCH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −8.3 (app t, $Ph_2PCH_2PPh_2$), −37.0 (app t, $Ph_2PCH_2PPh_2$).[10] ^1H NMR ($CDCl_3$) spectral data for **L-1**: δ 2.15 (s, 6H, $MeSCH_2SMe$), 3.61 (s, 2H, $MeSCH_2SMe$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.3 (s, $MeSCH_2SMe$), 40.1 (s, $MeSCH_2SMe$).[11]

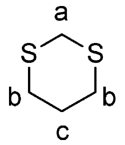
Preparation of Bis(benzylthio)methane (L-2). This reaction was carried out in a manner similar to that described above except that $PhCH_2Br$ was used. The products of *cis*-$[(dppm)_2RuBr_2]$ and bis(benzylthio)methane $[(PhCH_2S)_2CH_2]$ (**L-2**) were obtained in quantitative yields. ^1H NMR ($CDCl_3$) spectral data for *cis*-$[(dppm)_2RuBr_2]$: δ 4.79 (m, 2H, $Ph_2PCH_2PPh_2$), 5.09 (m, 2H, $Ph_2PCH_2PPh_2$), 6.46−8.25 (m, 40H, $Ph_2PCH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.4 (app t, $Ph_2PCH_2PPh_2$), −31.5 (app t, $Ph_2PCH_2PPh_2$).[10] ^1H NMR ($CDCl_3$) spectral data for **L-2**: δ 3.36 (s, 2H, $[(PhCH_2S)_2CH_2]$), 3.82 (s, 4H, $[(PhCH_2S)_2CH_2]$), 6.46−8.25 (m, 10H, $[(PhCH_2S)_2CH_2]$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.4 (s, $[(PhCH_2S)_2CH_2]$), 34.4 (s, $[(PhCH_2S)_2CH_2]$), 126.5−140.5 (m, $[(PhCH_2S)_2CH_2]$).[12]

Preparation of Bis(allylthio)methane (L-3). This reaction was also carried out in a manner similar to that described above except that $H_2C{=}CHCH_2Br$ was used. The products consisting of *cis*-$[(dppm)_2RuBr_2]$ and bis(allylthio)methane $[(H_2C{=}CHCH_2S)_2CH_2]$ (**L-3**) were obtained in quantitative yields. ^1H NMR ($CDCl_3$) spectral data for **L-3**: δ 3.25 (d, 4H, b, J(b,c) = 6.8 Hz), 3.57 (s, 2H, a), 5.11 (d, 2H, e, J(e,c) = 6.0 Hz), 5.15 (d, 2H, d, J(d,c) = 10.8 Hz), 5.76 (m, 2H, c). ^{13}C NMR ($CDCl_3$): δ 32.3 (s, a), 32.9 (s, b), 117.9 (s, c), 133.8 (s, d).



Preparation of 1,3-Dithianes (L-4, L-5). These reactions were performed in a manner similar to that described above except that $Br(CH_2)_2Br/Br(CH_2)_3Br$ were used. The *cis*-$[(dppm)_2RuBr_2]$ and the 1,3-dithianes were obtained in quantitative yields. ^1H NMR ($CDCl_3$) spectral data for 1,3-dithiane *c*-$SCH_2S(CH_2)_2$ (**L-4**): δ 3.88 (s, 2H, a), 3.17 (s, 4H, b). ^{13}C NMR ($CDCl_3$): δ 34.4 (s, b), 38.1 (s, a).[13] ^1H NMR ($CDCl_3$) spectral data for 1,3-dithiane *c*-$SCH_2S(CH_2)_3$ (**L-5**): δ 2.06 (m, 2H, c), 2.81 (t, 4H, b), 3.77 (s, 2H, a). ^{13}C NMR ($CDCl_3$): δ 26.6 (s, c), 29.9 (s, b), 31.9 (s, a).[14]





Preparation of $[(dppm)_2Ru(\eta^2\text{-}S(CH_3)CH_2S(CH_3))][OTf]_2$ (1). A solution of $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ (0.050 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with 2 equiv of MeOTf (12 μL, 0.10 mmol). An immediate color change from reddish brown to greenish-yellow took place. The resulting solution was stirred for 1 h, and then the volume was reduced to ca. 1 mL. The yellow product of $[(dppm)_2Ru(\eta^2\text{-}S(CH_3)CH_2S(CH_3))][OTf]_2$ (**1**) was precipitated by adding excess Et_2O, and the precipitate was washed with more Et_2O (3 × 5 mL) and dried in vacuo. Yield: 0.040 g (61%). ^1H NMR ($CDCl_3$, 263 K) spectral data for **1**: δ 1.05 (s, 6H, $MeSCH_2SMe$), 3.58 (d, 2H, J(H,H) = 8.8 Hz, $MeSCH_2SMe$), 4.95 (br s, 2H, $Ph_2PCH_2PPh_2$), 5.30 (br s, 2H, $Ph_2PCH_2PPh_2$), 6.34−8.46 (m, 40H, $Ph_2PCH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 263 K), ABCD spin system: δ −30.6 (d t, P_A, $J(P_A,P_B)$ = 321.2 Hz, $J(P_A,P_{av(C,D)})$ = 36.7 Hz), −20.3 (d t, P_B, $J(P_B,P_A)$ = 321.2 Hz, $J(P_B,P_{av(C,D)})$ = 25.2 Hz), −10.2 (m, P_C, $J(P_C,P_{av(A,B,D)})$ = 20.6 Hz), −6.9 (m, P_D, $J(P_D,P_{av(A,B,C)})$ = 17.2 Hz). ES-MS: m/z = 963 [M^+ − (Me + 2OTf)], 929 [M^+ − (Me + H_2S + 2OTf)].

Preparation of $[(dppm)_2Ru(\eta^2\text{-}c\text{-}SCH_2S(CH_2)_2)][OTf]_2$ (4). A solution of $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ (0.050 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with 2 equiv of $TfO(CH_2)_2OTf$ (0.034 g, 0.10 mmol) in benzene. An immediate color change from reddish brown to greenish-yellow was noted. The resulting solution was stirred for 1 h, and then the volume was reduced to ca. 1 mL. The yellow product of $[(dppm)_2Ru(\eta^2\text{-}c\text{-}SCH_2S(CH_2)_2)][OTf]_2$ (**4**) was precipitated by adding excess Et_2O, and the precipitate was washed with more Et_2O (3 × 5 mL) and dried in vacuo. Yield: 0.035 g (52%). ^1H NMR ($CDCl_3$, 233 K) spectral data for **4**: δ 1.03 (s, 4H, SCH_2S-

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(CH_2)$_2$), 3.55 (d, 2H, J(H,H) = 8.8 Hz, $MeSCH_2SMe$), 4.67 (br, 2H, $Ph_2PCH_2PPh_2$), 5.01 (br m, 2H, $Ph_2PCH_2PPh_2$), 6.23−8.51 (m, 40H, $Ph_2PCH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): δ −13.6 (app t, $Ph_2PCH_2PPh_2$, J(P,P) = 36.7 Hz), −7.3 (app t, $Ph_2PCH_2PPh_2$). ES-MS: m/z = 1125 [M^+ − OTf].

Preparation of [$(dppm)_2Ru(\eta^2$-*c*-$SCH_2S(CH_2)_3$)][OTf]$_2$ (5a). A solution of [$(dppm)_2Ru(\eta^2$-S_2CH_2)] (0.050 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with 2 equiv of $TfO(CH_2)_3OTf$ (0.035 g, 0.10 mmol) in benzene. An immediate color change from reddish brown to greenish-yellow was observed. The resulting solution was stirred for 1 h, and then the volume was reduced to ca. 1 mL. The yellow product of [$(dppm)_2Ru(\eta^2$-*c*-$SCH_2S(CH_2)_3$)][OTf]$_2$ (**5a**) was precipitated by adding excess Et_2O, and the precipitate was washed with more Et_2O (3 × 5 mL) and dried in vacuo. Yield: 0.042 g (63%). ^1H NMR ($CDCl_3$, 263 K) spectral data for **5a**: δ 1.35 (qnt, 2H, $SCH_2S(CH_2CH_2CH_2)$), 2.84 (d m, 4H, $SCH_2S(CH_2CH_2CH_2)$), 3.54 (d, 2H, J(H,H) = 8.8 Hz, $MeSCH_2SMe$), 4.92 (br s, 2H, $Ph_2PCH_2PPh_2$), 5.32 (br s, 2H, $Ph_2PCH_2PPh_2$), 6.34−8.45 (m, 40H, $Ph_2PCH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 263 K), ABCD spin system: δ −30.4 (d t, P_A, $J(P_A,P_B)$ = 321.2 Hz, $J(P_A,P_{av(C,D)})$ = 36.7 Hz), −20.6 (d t, P_B, $J(P_B,P_A)$ = 321.2 Hz, $J(P_B,P_{av(C,D)})$ = 25.2 Hz), −10.5 (m, P_C, $J(P_C,P_{av(A,B,D)})$ = 17.2 Hz), −7.2 (m, P_D, $J(P_D,P_{av(A,B,C)})$ = 19.3 Hz). ES-MS: m/z = 963 [M^+ − (C_2H_4 + 2OTf)], 929 [M^+ − (C_2H_4 + H_2S + 2OTf)].

In another experiment, the crude product from the reaction of [$(dppm)_2Ru(\eta^2$-S_2CH_2)] and $Br(CH_2)_3Br$ consisting of a mixture of [$(dppm)_2Ru(\eta^2$-*c*-$SCH_2S(CH_2)_3$)][Br]$_2$ (**5b**) and *cis*-[$(dppm)_2RuBr_2$] was analyzed by mass spectroscopy. ES-MS: m/z = 1071 [M^+ − Br], 963 [M^+ − (C_2H_4 + 2Br)], 929 [M^+ − (C_2H_4 + H_2S + 2Br)].

Preparation of *trans*-[$(dppe)_2Ru(H)(SC(SH)H)$][BF_4] (6). To a $CDCl_3$ solution (0.6 mL) of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] (0.015 g, 0.015 mmol) in a 5 mm NMR tube was added $HBF_4\cdot Et_2O$ (1 equiv, 2 μL, 0.015 mmol), and the solution was shaken well. The color of the reaction mixture turned from yellow to red immediately. Attempts to isolate the product *trans*-[$(dppe)_2Ru(H)(SC(SH)H)$][BF_4] (**6**) resulted in its decomposition; therefore, it was characterized using NMR spectroscopy only. ^1H NMR ($CDCl_3$) spectral data for **6**: δ −12.25 (qnt, 1H, Ru−H, $J(H,P_{cis})$ = 18.6 Hz), 2.31 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.81 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 5.78 (d, 1H, $SC(SH)H$, ^3J(H,H) = 13.7 Hz), 6.52−7.42 (m, 40H, $Ph_2PCH_2CH_2PPh_2$), 7.69 (d, 1H, $SC(SH)H$, ^3J(H,H) = 13.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.1 (qnt, $Ph_2PCH_2CH_2PPh_2$), 125.3−137.9 (m, $Ph_2PCH_2CH_2PPh_2$), 210.7 (s, $SC(SH)H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.4 (s, $Ph_2PCH_2CH_2PPh_2$).

Preparation of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CCH{=}CH_2)H)$][$BPh_4$] (7). A THF solution (10 mL) of $NaBPh_4$ (0.140 g, 0.40 mmol) and allyl bromide (30 μL, 0.40 mmol) was added to a THF solution (10 mL) of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] (0.200 g, 0.200 mmol). An immediate color change from yellow to orange was noted. The reaction mixture was stirred for 10 min, and then the volatiles were removed under vacuo. The resulting orange solid was redissolved in 10 mL of CH_2Cl_2, the solution was filtered, and the volume of the filtrate was reduced to ca. 2 mL. The product of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CCH{=}CH_2)H)$][$BPh_4$] (**7**) was precipitated by adding excess Et_2O and dried in vacuo. Yield: 0.210 g (79%). Anal. Calcd for $C_{80}H_{75}BP_4RuS_2\cdot$THF: C, 71.57; H, 5.93. Found: C, 71.83; H, 5.65 (the presence of a molecule of THF was confirmed using ^1H NMR spectroscopy). ^1H NMR ($CDCl_3$) spectral data for **7**: δ −12.65 (qnt, 1H, Ru-H, $J(H,P_{cis})$ = 18.6 Hz), 2.23 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.69 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 3.28 (d, 2H, $SC(SH_2CCH{=}CH_2)H$, J(H,H) = 6.8 Hz), 5.00 (d, 1H, $SC(SH_2CCH{=}CH_2)H$, J(H,H) = 16.6 Hz), 5.08 (d, 1H, $SC(SH_2CCH{=}CH_2)H$, J(H,H) = 16.6 Hz), 5.41 (m, 1H, $SC(SH_2CCH{=}CH_2)H$), 6.55−7.63 (m, 40H, $Ph_2PCH_2CH_2PPh_2$), 6.55−7.63 (m, 20H, BPh_4), 7.98 (s, 1H, $SC(SH_2CCH{=}CH_2)H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.3 (qnt, $Ph_2PCH_2CH_2PPh_2$), 37.2 (s, $SC(SH_2CCH{=}CH_2)H$), 120.2 (s, $SC(SH_2CCH{=}CH_2)H$), 121.7−136.3 (m, $Ph_2PCH_2CH_2PPh_2$), 130.4 (s, $SC(SH_2CCH{=}CH_2)H$), 164.3 (q, BPh_4), 213.7 (s, $SC(SH_2CCH{=}CH_2)H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.4 (s, $Ph_2PCH_2CH_2PPh_2$).

Preparation of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CC_6H_5)H)$][$BPh_4$] (8). This compound was prepared in a manner similar to that of the allyl dithioformate analogue described above except that benzyl bromide was used. Yield: 73%. Anal. Calcd for $C_{84}H_{77}BP_4RuS_2\cdot$THF: C, 72.46; H, 5.87. Found: C, 72.70; H, 5.59 (the presence of a molecule of THF was confirmed using ^1H NMR spectroscopy). ^1H NMR ($CDCl_3$) spectral data for *trans*-[$(dppe)_2Ru(H)(SC(SH_2CC_6H_5)H)$][$BPh_4$] (**8**): δ −12.64 (qnt, 1H, Ru−H, $J(H,P_{cis})$ = 18.6 Hz), 2.21 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.65 (br s, 4H, $Ph_2PCH_2CH_2PPh_2$), 3.98 (s, 2H, $SC(SH_2CC_6H_5)H$), 6.52−7.40 (m, 40H, $Ph_2PCH_2CH_2PPh_2$), 8.01 (s, 1H, $SC(SH_2CC_6H_5)H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.0 (qnt, $Ph_2PCH_2CH_2PPh_2$), 38.9 (s, $SC(SH_2CC_6H_5)H$), 121.6−136.3 (m, $Ph_2PCH_2CH_2PPh_2$), 164.3 (q, BPh_4), 211.6 (s, $SC(SH_2CC_6H_5)H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.4 (s, $Ph_2PCH_2CH_2PPh_2$).

Reaction of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CCH{=}CH_2)H)$][$BPh_4$] (7) with CH_3CN. A CH_2Cl_2 solution (10 mL) of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CCH{=}CH_2)H)$][$BPh_4$] (**7**) (0.500 g, 0.370 mmol) was treated with 5 equiv of CH_3CN (98 μL, 1.850 mmol), and the resulting solution was stirred for 15 min. During this time, the color of the solution turned from orange to yellow. Then the solution was subjected to vacuum distillation and the free allyldithioformate (**L-7**) was fractionally collected in a liquid-N_2 trap and characterized. ^1H NMR ($CDCl_3$) spectral data for **L-7**: δ 3.99 (m, 2H, $SC(SH_2CCH{=}CH_2)H$), 5.23 and 5.35 (two d, 2H, $SC(SH_2CCH{=}CH_2)H$), 5.85 (m, 1H, $SC(SH_2CCH{=}CH_2)H$), 11.25 (s, 1H, $SC(SH_2CCH{=}CH_2)H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.1 (s, $SC(SH_2CCH{=}CH_2)H$), 120.0 (s, $SC(SH_2CCH{=}CH_2)H$), 130.8 (s, $SC(SH_2CCH{=}CH_2)H$), 217.2 (s, $SC(SH_2CCH{=}CH_2)H$).[15] IR (CH_2Cl_2; cm^{-1}): 1108 (ν(C═S)). Electronic spectrum: 307 nm.

In another experiment, after the addition of CH_3CN and stirring for 15 min, the volume of the solution was reduced and the product of *trans*-[$(dppe)_2Ru(H)(CH_3CN)$][BPh_4] was precipitated by the addition of excess Et_2O. It was dried in vacuo. Yield: 0.400 g (85%). ^1H NMR ($CDCl_3$) spectral data for *trans*-[$(dppe)_2Ru(H)(CH_3CN)$][BPh_4]: δ −15.98 (qnt, 1H, Ru−H, $J(H,P_{trans})$ = 18.6 Hz), 0.96 (s, 3H, CH_3CN), 2.00 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 2.41 (m, 4H, $Ph_2PCH_2CH_2PPh_2$), 6.56−7.44 (m, 40H, $Ph_2PCH_2CH_2PPh_2$), 6.56−7.44 (m, 20H, BPh_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 65.1. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.7 (s, CH_3CN), 31.6 (qnt, $Ph_2PCH_2CH_2PPh_2$), 121.7−136.3 (m, $Ph_2PCH_2CH_2PPh_2$), 164.2 (q, BPh_4), 123.1 (s, CH_3CN).

Reaction of *trans*-[$(dppe)_2Ru(H)(SC(SH_2CC_6H_5)H)$][$BPh_4$] (8) with CH_3CN. This reaction was carried out in a manner similar to that described in the case of allyl dithioformate hydride complex. The product of benzyl dithioformate (**L-8**) was fractionally distilled and characterized. ^1H NMR ($CDCl_3$) spectral data for **L-8**: δ 4.56 (s, 2H, $SC(SH_2CC_6H_5)H$), 6.52−7.40 (m, 5H, $SC(SH_2CC_6H_5)H$), 11.28 (s, 1H, $SC(SH_2CC_6H_5)H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.8 (s, $SC(SH_2CC_6H_5)H$), 121.6−136.3 (s, $SC(SH_2CC_6H_5)H$), 217.0 (s, $SC(SH_2CC_6H_5)H$).[16]

Preparation of *trans*-[$(dppe)_2Ru(H)(SC(S(CH_2)_3OTf)H)$][OTf] (9). A solution of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] (0.100 g, 0.10

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(15) Allyl dithioformate has not been reported in the literature.

(16) The NMR data matched with the data reported in the literature: Sanchez, S.; Bateson, J. H.; O'Hanlon, P. J.; Gallagher, T. *Org. Lett.* **2004**, *6*, 2781−2783.

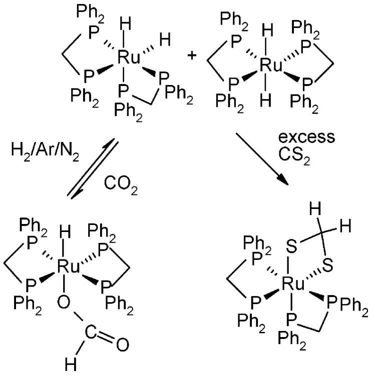
mmol) in CH_2Cl_2 (5 mL) was treated with 5 equiv of $TfO(CH_2)_3OTf$ (0.170 g, 0.5 mmol) in benzene. An immediate color change from yellow to red took place. The resulting solution was stirred for 10 min, and then the volume was reduced to ca. 1 mL. The product of *trans*-[(dppe)$_2$Ru(H)(SC(S(CH$_2$)$_3$OTf)H)][OTf] (**9**) was precipitated by adding excess Et_2O, and the precipitate was washed with more Et_2O (3 × 5 mL) and dried in vacuo. Yield: 0.09 g, 67%. Anal. Calcd for $C_{58}H_{56}F_6O_6P_4RuS_4$: C, 52.88; H, 4.28. Found: C, 52.21; H, 4.94. ^1H NMR ($CDCl_3$) spectral data for **9**: δ −12.63 (qnt, 1H, Ru−*H*, $J(H,P_{trans}) = 18.6$ Hz), 2.30 (br s, 4H, Ph$_2$PC*H*$_2$C*H*$_2$PPh$_2$), 2.85 (br s, 4H, Ph$_2$PC*H*$_2$C*H*$_2$PPh$_2$), 3.19 (t, 2H, SC(SC*H*$_2$CH$_2$CH$_2$OTf)H), 3.55 (t, 2H, SC(SCH$_2$CH$_2$C*H*$_2$OTf)H), 2.14 (qnt, 2H, SC(SCH$_2$C*H*$_2$CH$_2$OTf)H), 7.89 (s, 1H, SC(SCH$_2$CH$_2$CH$_2$OTf)*H*), 6.61−7.37 (m, 40H, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.2 (s, SC(SCH$_2$*C*H$_2$CH$_2$OTf)H), 32.6 (s, SC(SCH$_2$CH$_2$*C*H$_2$OTf)H), 32.1 (s, SC(S*C*H$_2$CH$_2$CH$_2$OTf)H), 33.4 (qnt, Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 127.9−132.8 (m, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$), 212.7 (s, S*C*(SCH$_2$CH$_2$CH$_2$OTf)H), 133.2 (qnt, SC(SCH$_2$CH$_2$CH$_2$*OTf*)H), 135.7 (qnt, [*OTf*]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.9 (s, Ph$_2$*P*CH$_2$CH$_2$*P*Ph$_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −72.7 (s, 3F, SC(SCH$_2$CH$_2$CH$_2$*OTf*)H), −72.8 (s, 3F, free [*OTf*]$^-$ (counterion)).

Preparation of *trans*-[(dppe)$_2$Ru(H)(SC(S(CH$_2$)$_4$OTf)H)][OTf] (10). A solution of *trans*-[(dppe)$_2$Ru(H)(SC(S)H)] (0.100 g, 0.10 mmol) in CH_2Cl_2 (5 mL) was reacted with 5 equiv of $TfO(CH_2)_4OTf$ (0.180 g, 0.5 mmol) in benzene. The solution color turned from yellow to red immediately. It was stirred for 10 min, and then the volume was reduced to ca. 1 mL. The product of *trans*-[(dppe)$_2$Ru(H)(SC(S(CH$_2$)$_4$OTf)H)][OTf] (**10**) was precipitated by adding excess Et_2O, and the precipitate was washed with more Et_2O (3 × 5 mL) and dried in vacuo. Yield: 0.085 g, 62%. Anal. Calcd for $C_{59}H_{58}F_6O_6P_4RuS_4$: C, 53.22; H, 4.39. Found: C, 52.49; H, 4.19. ^1H NMR ($CDCl_3$) spectral data for **10**: δ −12.71 (qnt, 1H, Ru−*H*, $J(H,P_{trans}) = 18.6$ Hz), 2.30 (br s, 4H, Ph$_2$PC*H*$_2$C*H*$_2$PPh$_2$), 2.83 (br s, 4H, Ph$_2$PC*H*$_2$C*H*$_2$PPh$_2$), 2.96 (t, 2H, SC(SC*H*$_2$CH$_2$ CH$_2$CH$_2$OTf)H), 3.52 (t, 2H, SC(SCH$_2$CH$_2$CH$_2$C*H*$_2$OTf)H), 1.74 (qnt, 2H, SC(SCH$_2$ CH$_2$C*H*$_2$CH$_2$OTf)H), 1.97 (qnt, 2H, SC(SCH$_2$CH$_2$C*H*$_2$CH$_2$OTf)H), 7.96 (s, 1H, SC(SCH$_2$CH$_2$CH$_2$OTf)*H*), 6.61−7.37 (m, 40H, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.9 (s, SC(SCH$_2$*C*H$_2$*C*H$_2$CH$_2$OTf)H), 31.5 (s, SC(S*C*H$_2$CH$_2$CH$_2$*C*H$_2$OTf)H), 33.3 (qnt, Ph$_2$P*C*H$_2$*C*H$_2$PPh$_2$), 127.9−132.8 (m, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$), 213.4 (s, S*C*(SCH$_2$CH$_2$CH$_2$CH$_2$OTf)H), 133.3 (qnt, SC(SCH$_2$CH$_2$CH$_2$*OTf*)H), 135.7 (qnt, [*OTf*]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.91 (s, Ph$_2$*P*CH$_2$CH$_2$*P*Ph$_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −72.7 (s, 3F, SC(SCH$_2$CH$_2$CH$_2$*OTf*)H), −72.8 (s, 3F, free [*OTf*]$^-$ (counterion)).

Results and Discussion

Preparation of Bis(alkylthio)methanes and 1,3-Dithianes. Solutions of *cis*-/*trans*-[(dppm)$_2$Ru(H)$_2$] in C_6D_6/toluene react with CO_2 (1 atm) and CS_2 (1 or 2 equiv) to give the insertion products *trans*-[(dppm)$_2$Ru(H)(OC(O)H)] and a mixture of *cis*- and *trans*-[(dppm)$_2$Ru(H)(SC(S)H)], respectively. Attempts to hydrogenate the hydride formate derivative only resulted in the recovery of the starting dihydride complex via the deinsertion of CO_2. On the other hand, when the mixture of *cis*- and *trans*-[(dppm)$_2$Ru(H)(SC(S)H)] was allowed to crystallize, a new species was formed that was identified by NMR spectroscopy and X-ray crystallography as [(dppm)$_2$Ru(η^2-S$_2$CH$_2$)]. This species is a result of a unique double insertion of CS_2 into two Ru−H bonds. When excess CS_2 was used, the methanedithiolate complex was isolated as a major product in good yield (Scheme 1).[2]

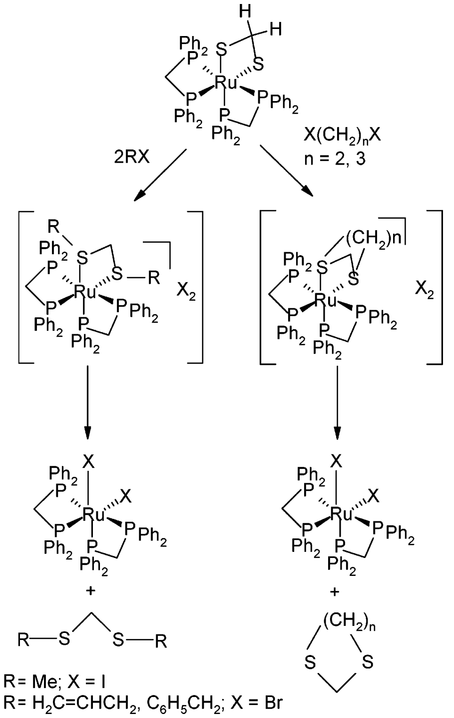
Scheme 1



The methanedithiolate complex provides an opportunity for functionalizing the inserted CS_2 due to the virtue of the accessibility of the lone pairs on both the sulfur atoms. We reacted the methanedithiolate moiety with electrophilic reagents such as RX (R = Me, X = I; R = $H_2C{=}CHCH_2$, X = Br; R = $C_6H_5CH_2$, X = Br) and XRX (R = $(-CH_2-)_2$, X = Br; R = $(-CH_2-)_3$, X = Br) and monitored the reactions using NMR spectroscopy. The added electrophile (RX) attacks both the sulfur atoms resulting in a bis(alkylthio)methane derivative [(dppm)$_2$Ru(η^2-S(R)CH$_2$S(R)]-[X]$_2$ that we have not been able to isolate; we, however, have observed this species using NMR spectroscopy. Over a period of time at room temperature, the bis(alkylthio)methane, RSCH$_2$SR (R = Me (**L-1**), $C_6H_5CH_2$ (**L-2**), $H_2C{=}CHCH_2$ (**L-3**)), gets eliminated and the halide counterions bind to the metal center giving *cis*-[(dppm)$_2$RuX$_2$]. Both the species were obtained in quantitative yields. In the reaction of the [(dppm)$_2$Ru(η^2-S$_2$CH$_2$)] with alkyl dihalides (XRX), derivatives with 1,3-dithianes bound to the metal center of the type [(dppm)$_2$Ru(η^2-*c*-SCH$_2$S(CH$_2$)$_n$)][X]$_2$ (n = 2, 3) were observed spectroscopically. The 1,3-dithiane moieties (**L-4**, **L-5**) get eliminated from the metal complex over a period of time leaving behind the *cis*-[(dppm)$_2$RuX$_2$] complex. In these cases also, both 1,3-dithiane and the ruthenium halide complex were obtained in quantitative yields. These reactions have been summarized in Scheme 2.

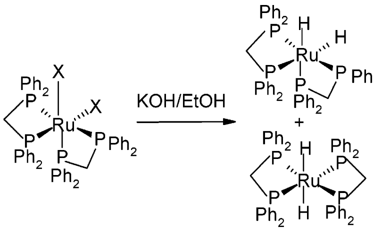
To our knowledge, transition metal complexes bearing bis(alkylthio)methane or 1,3-dithiane as ligands are unprecedented. Our attempts to isolate the [(dppm)$_2$Ru(η^2-S(R)CH$_2$S(R))][X]$_2$ or the [(dppm)$_2$Ru(η^2-*c*-SCH$_2$S(CH$_2$)$_n$)][X]$_2$ (n = 2, 3) complexes afforded only the dihalide *cis*-[(dppm)$_2$RuX$_2$] suggesting that these neutral sulfur ligands are extremely loosely bound to the metal center and are quite labile. We also attempted to employ a slightly different strategy by using a sterically congested and noncoordinating counterion such as OTf to prevent the elimination of the sulfur ligand and the subsequent binding of the counterion to the metal center. Our attempts were successful in the isolation of [(dppm)$_2$Ru(η^2-S(CH$_3$)CH$_2$S(CH$_3$))][OTf]$_2$ (**1**) and [(dppm)$_2$Ru(η^2-*c*-SCH$_2$S(CH$_2$)$_n$)][OTf]$_2$ (n = 2 (**4**), 3 (**5**)) derivatives; however, the purification procedures to obtain samples pure enough for elemental analyses resulted in certain decomposed material. Nevertheless, the crude prod-

Scheme 2



ucts could be characterized by both NMR (at low temperatures) and mass spectroscopy. We found that some of the NMR resonances of these products at room temperature were broadened, whereas at low temperatures they resolve and the spectral assignments could be made without any ambiguity. We are currently investigating the origin of the broadening of the NMR signals. The NMR resonances not belonging to those of the products in the crude materials could not be assigned. The NMR spectral features of the isolated [(dppm)$_2$Ru(η^2-S(CH$_3$)CH$_2$S(CH$_3$))]$^{2+}$ (cation of **1**) and [(dppm)$_2$Ru(η^2-*c*-SCH$_2$S(CH$_2$)$_n$)][X]$_2$ (n = 2 (**4**), 3 (**5**)) complexes matched those of the in-situ generated bis(alkylthio)methane and 1,3-dithiane complexes.

The unique feature of the reaction sequence presented in Scheme 2 is that it affords an opportunity to recycle the starting ruthenium dihydride *cis*-/*trans*-[(dppm)$_2$Ru(H)$_2$] from the dihalide complex *cis*-[(dppm)$_2$RuX$_2$]. When *cis*-[(dppm)$_2$RuX$_2$] was reacted with KOH/EtOH, *cis*-/*trans*-[(dppm)$_2$Ru(H)$_2$] was obtained in a yield of 48% (eq 1).[8]



(1)

We attempted to generate a methanedithiol complex [(dppm)$_2$Ru(η^2-S(H)CH$_2$S(H))][BF$_4$]$_2$ by reacting [(dppm)$_2$Ru(η^2-S$_2$CH$_2$)] with 2 equiv of HBF$_4$·Et$_2$O. An instantaneous reaction was apparent; however, NMR spectroscopy of the products did not reveal the presence of a dithiol species. We speculate that the dithiol complex, if at all formed, could be expected to release the free methane dithiol, it being a weakly binding ligand. This further results in other side reactions in addition to generating certain decomposed material. The NMR spectra of the reaction mixture indicated complex mixtures of products thus precluding the specific characterization of the dithiol complex.

Caserio and co-workers[11a] prepared bis(methylthio)methane (**L-1**) earlier in high yield in quite a laborious process using MeSH as one of the starting materials. Tanikaga et al.[17] obtained bis(methylthio)methane in moderate yields starting from Me$_2$S. Although bis(allylthio)methane (**L-3**) has been reported in the literature, there exists no characterization data.[18] By using the pathway shown in Scheme 2, we have been able to isolate bis(allylthio)methane and characterize it. The NMR spectral assignments were made on the basis of a ^{1}H$-^1$H COSY experiment. Kuhn and Schumann[12] reported the preparation of bis(benzylthio)methane using thiol as one of the starting materials; in addition, they also made an iron derivative using this species. The 1,3-dithiane *c*-SCH$_2$S(CH$_2$)$_2-$ (**L-4**) has been prepared in a low yield via condensation of paraform (or paraldehyde) with 1,2-ethanedithiol.[13] On the other hand, Kutateladze and co-workers reported a one-pot synthesis of 1,3-dithiane *c*-SCH$_2$S(CH$_2$)$_3-$ (**L-5**) in 83% yield using CS$_2$ and NaBH$_4$.[14] Our routes to obtain the bis(alkylthio)methanes and the 1,3-dithianes are quite facile, and in all the cases, the yields were quantitative. In these respects, the pathways presented here are better than those available in the literature.

Open-chain bis(alkylthio)methanes, which are also known as 1,3-dithioacetals, especially bis(methylthio)methane, are used in the synthesis of carbocycles[19] and certain heterocycles.[20] Unlike cyclic dithioacetals which have steric constraints, bis(methylthio)methane is sterically unbiased and is also used extensively in carbohydrate chemistry.[21] Bis(benzylthio)methane and bis(allylthio)methane are used as a ligand[22] and in the synthesis of allylsilanes,[23] respectively. Bis(alkylthio)methanes also have a special place in organic synthesis; they are used as reagents for C$-$C bond formation and carbonyl addition reactions.[24] In addition, the 1,3-dithiane (*c*-SCH$_2$S(CH$_2$)$_3-$), a six-membered cyclic dithioacetal, is used extensively as a good nucleophile[25] and an efficient

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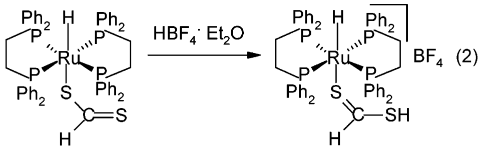
Michael donor.[26] On the other hand, its five-membered counterpart (*c*-$SCH_2S(CH_2)_2-$) has found fewer occurrences in organic synthesis; this compound also undergoes nucleophilic addition[27] and radical addition to alkenes.[28]

Preparation and Characterization of the Dithioformic Acid Complex of Ruthenium. The addition of CS_2 to the sterically impeding *cis*-[$(dppe)_2Ru(H)_2$] in toluene solution resulted in a quantitative yield of the dithioformate derivative *trans*-[$(dppe)_2Ru(H)(SC(S)H)$]. This compound under thermal conditions in toluene gave the double-inserted methane dithiolate complex [$(dppe)_2Ru(\eta^2\text{-}S_2CH_2)$] as in the dppm analogue.[2] This reaction was not found to be as clean as in the case of the dppm complex, perhaps due to the sterically encumbered diphosphine ligand leading to certain unidentified decomposed material in addition to the methanedithiolate complex.

Dithioformic acid (**L-6**), an unstable molecule and a potential interstellar species, has been studied extensively by theoretical methods[29] and microwave[30] and IR spectroscopy.[31] Addition of 2 equiv of $HBF_4 \cdot Et_2O$ to a chloroform solution of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] resulted in an instantaneous reaction to afford an unprecedented example of a dithioformic acid complex of a transition metal, *trans*-[$(dppe)_2Ru(H)(SC(H)SH)$][BF_4] (**6**) (eq 2). Our attempts to isolate this derivative in the solid state only gave certain decomposed material as evidenced by NMR spectroscopy. The dithioformic acid complex was found to be stable in solution for extended periods of time (2−3 days) without undergoing any decomposition. The complex **6** shows a quintet at δ −12.23 for the hydride and two broad singlets at δ 5.78 and 7.69, respectively, one each for the SH and SCH fragments of the dithioformic acid in the ^1H NMR spectrum. The two broad singlets for the dithioformic acid resolve into doublets at low temperatures with $^3J(H,H) = 13.7$ Hz. The $^{31}P\{^1H\}$ NMR spectrum shows only one singlet at δ 63.4 indicating that all the four P atoms are equivalent. It is interesting to compare the reactivity of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] and a somewhat analogous osmium derivative [$(P^iPr_3)_2Os(H)(CO)(\eta^2\text{-}S_2CH)$][32] with $HBF_4 \cdot Et_2O$. In the case of the osmium complex, protonation in CD_2Cl_2 gave the corresponding dihydrogen complex, and in Et_2O solvent, the site of protonation was the dithioformate to afford the methane dithiolate derivative. The lone pairs of electrons on the sulfur atoms were unaffected in the protonation reaction.



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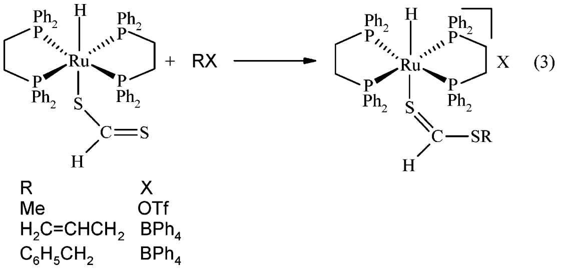
Preparation of Alkyl Dithioformates. The dithioformate moiety of *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] can be functionalized using various electrophilic reagents such as RX (R = Me, X = OTf; R = $H_2C{=}CHCH_2$, X = BPh_4; R = $C_6H_5CH_2$, X = BPh_4) affording the corresponding alkyl dithioformate derivatives (eq 3). The methyldithioformate complex *trans*-[$(dppe)_2Ru(H)(SC(SMe)H)$][OTf] has been crystallographically characterized,[3] whereas the others were characterized by NMR spectroscopy.



We found that the alkyl dithioformate complexes *trans*-[$(dppe)_2Ru(H)(SC(SR)H)$][X] can be isolated in the solid state and can be characterized provided the counterions are bulky and noncoordinating type, e.g., OTf and BPh_4. The free alkyl dithioformates can be released from the respective complexes via substitution of the alkyl dithioformate by (a) H_2 or (b) CH_3CN. In the substitution with H_2 the free alkyl dithioformates were obtained only in small quantities whereas, with CH_3CN, the free esters were obtained in quantitative yields. In both of these pathways, the resulting hydride complexes, *trans*-[$(dppe)_2Ru(H)(\eta^2\text{-}H_2)$]$^+$ and *trans*-[$(dppe)_2Ru(H)(CH_3CN)$]$^+$, are dead ends from where the starting ruthenium dihydride complex *cis*-[$(dppe)_2Ru(H)_2$] cannot be recovered.

Thus, using the above protocol, we were able to isolate the free esters, methyl dithioformate, allyl dithioformate (**L-7**), and benzyl dithioformate (**L-8**), and characterize them spectroscopically. Gallagher et al.[16] synthesized benzyl dithioformate by direct thionation of the corresponding thioformate ($PhCH_2SC(O)H$)[33] using Lawesson's reagent. Both methyl and benzyl dithioformates are potential 1,3-dipolarophiles and have been utilized to synthesize C(2)-unsubstituted penems from β-lactam-based oxazolidinones.

We employed a slightly different strategy for the recovery of the starting ruthenium dihydride complex. When *trans*-[$(dppe)_2Ru(H)(SC(S)H)$] was reacted with the simple alkyl halides (MeI, $H_2C{=}CHCH_2Br$, or $C_6H_5CH_2Br$), the free alkyl

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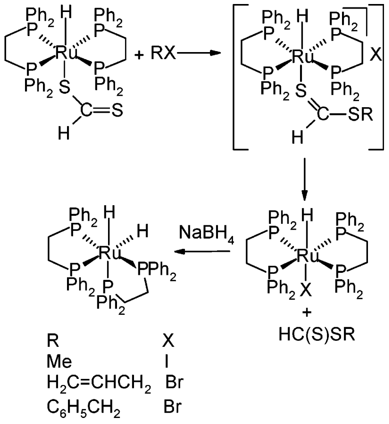
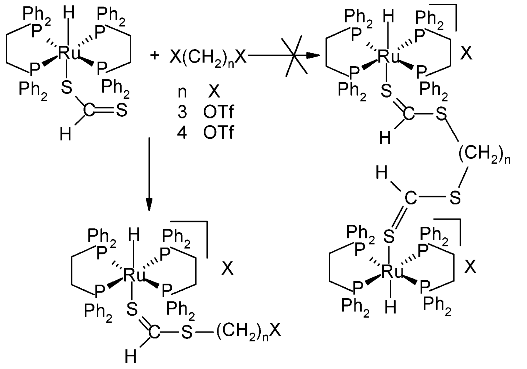
Scheme 3



dithioformate and *trans*-[(dppe)$_2$Ru(H)X] (X = I or Br) were obtained in a very facile reaction via the intermediacy of *trans*-[(dppe)$_2$Ru(H)(SC(SR)H)][X] that was observed NMR spectroscopically (Scheme 3). The starting *cis*-[(dppe)$_2$Ru(H)$_2$] was recovered via reaction of *trans*-[(dppe)$_2$Ru(H)X] with NaBH$_4$ in a THF−methanol solution. Thus, by employing a good coordinating ligand as the counterion in the hydride alkyl dithioformate complex, it is possible to obtain a precursor from which the ruthenium dihydride complex *cis*-[(dppe)$_2$Ru(H)$_2$] could be recovered.

Reaction of Hydride Dithioformate Complex with XRX. In an attempt to prepare bimetallic complexes using a linker, e.g., [(dppe)$_2$Ru(H)(SCH(S)(CH$_2$)$_n$(S)HCS)(H)Ru(dppe)$_2$]$^{2+}$, we examined the reactivity of the dithioformate complex with alkaneditriflates. Solutions of *trans*-[(dppe)$_2$Ru(H)(SC(S)H)] in CH$_2$Cl$_2$ react with 5 equiv of propaneditriflate OTf−(CH$_2$)$_3$−OTf or butaneditriflate OTf−(CH$_2$)$_4$−OTf to afford the respective ruthenium derivatives *trans*-[(dppe)$_2$Ru(H)(SC(S(CH$_2$)$_3$OTf)H)][OTf] (**9**) and *trans*-[(dppe)$_2$Ru(H)(SC(S(CH$_2$)$_4$OTf)H)][OTf] (**10**). No bimetallic complexes were obtained. In addition, the isolated products were accompanied by a few other unidentifiable species and purification proved to be difficult. When the same reactions were carried out using the respective halides, the derivatized species were observed as intermediates; however, the isolation of the products was accompanied by a few other compounds. Thus, the strategy of employing bulky, noncoordinating counterions proved successful in isolating these novel species in the solid state (Scheme 4).

Scheme 4



Conclusions

In conclusion, CS$_2$ has been inserted into M−H bonds of ruthenium dihydride complexes to obtain either methanedithiolate or dithioformate derivatives. The methanedithiolate moiety can be functionalized using various electrophiles, and the corresponding organic compounds, e.g., bis(alkylthio)methanes or 1,3-dithianes, could be obtained in quantitative yield. On the other hand, the dithioformate species can also be functionalized using various electrophiles and the corresponding organic moieties were obtained in quantitative yields. In both of these pathways, the starting ruthenium dihydride complexes have been regenerated thus making the processes attractive. Thus, CS$_2$ has been used as a source of the C$_1$ synthetic unit for the generation of useful organic compounds.

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Supporting Information Available: NMR stack plots of the reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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