REACTIONS OF SULFINYL CARBANIONS WITH ORGANOMETALLIC COMPOUNDS: PREPARATION OF (η^5-C$_5$H$_5$)$_2$TiCH$_2$SC$_6$H$_4$

C.R. LUCAS

*Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7 (Canada)*

Summary

Sulfinyl carbanions, [RS(O)CHR′]$^-$Li$^+$ (R = Ph, Me; R′ = H, Ph) have been observed to have often low reactivity towards neutral transition metal organometallic systems. When reactions do occur they usually involve salt eliminations and formation of complex mixtures containing inter alia organic sulfides, disulfides, freed ligands or their oxides and reduced forms of the organometallic reactants. From the sulfinyl ylide [PhS(O)CH$_2$]Li, *exo-*[η^5-C$_6$H$_6$CH$_2$S(O)Ph]Mn-(CO)$_3$ and the new metallocyclic compound (η^5-C$_5$H$_5$)$_2$TiCH$_2$SC$_6$H$_4$ have been prepared, some properties of the latter examined and its sulfonium derivative [(η^5-C$_5$H$_5$)$_2$TiCH$_2$S(Me)C$_6$H$_4$]BF$_4$ isolated.

Introduction

Since first prepared by Corey and Chaykovsky [1,2] many applications of sulfinyl carbanions (eq. 1) to organic synthesis have been documented [3—5].

$$\tag{1}$$
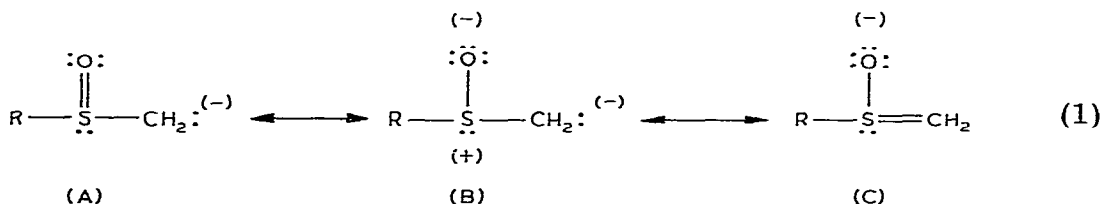
Little use however has been made of these ylides as reagents in organometallic synthesis. The purpose of this work therefore was to explore their reactions with organometallic compounds of the transition metals.

Results and discussion

General

The ylides examined in this work were [RS(O)CHR′]Li (R = Me or Ph and R′ = H or Ph). In general, they were found to have low reactivities with organometallic compounds. The only exceptions to this rule occurred when salt elimination or nucleophilic attack on a cation was possible. For example, when *Cp$_2$Co, (Ph$_3$P)$_2$Rh(CO)Cl, Cp$_2$Ni, Cp$_2$Zr(H)Cl, Cp$_2$ZrCl$_2$, CpV(CO)$_4$, *BzCr(CO)$_3$ Cp$_2$NbCl$_2$ or [Cp$_2$Co]Br were treated in tetrahydrofuran at room temperature with the ylides, no reactions were observed and the organometallic starting materials were recovered unchanged. Clearly, the ylide-carbanions have lower nucleophilicity than might be expected although whether this is due to Cp$_\pi$ → Sd$_\pi$ bonding or some other charge delocalization process is currently a matter of dispute [6].

When ylide reactions did occur, they usually involved salt eliminations and formation of complex mixtures containing inter alia sulfides, disulfides, freed ligands or their oxides and reduced forms of the organometallic reactants. For example [PhS(O)CH$_2$]Li, which is typical of all the carbanions used in this study, reacts with [CpFe(CO)$_2$PPh$_3$]Cl to yield LiCl, [CpFe(CO)$_2$]$_2$, PhSSPh, PHSCH$_2$CH$_2$SPh, PhSCH$_2$SPh, Ph$_3$P and Ph$_3$P=O. Reactions of Mn(CO)$_5$Br, CpFe(CO)$_2$Cl, CpFe(CO)[P(OPh)$_3$]Cl, CpFe[P(OPh)$_3$]$_2$Cl, Cp$_2$VCl$_2$, Cu(acac)$_2$**, (Et$_3$P)$_2$NiCl$_2$ and Cp$_2$TiCl$_2$ were similar in the sense that good yields of the eliminated salt were obtained together with mixtures of (RSCHR′)$_2$, (RS)$_2$CHR′ and RSSR among other products.

· Since the components of these mixtures are usually readily available by other more efficient processes, these reactions are of limited synthetic value except in the cases discussed later.

The mechanism of these reactions has not been examined in detail but the type of products suggests involvement by carbon-centred α-sulfinyl or α-thio radicals. This suggestion is supported by the following observations. Solutions of the ylides alone under otherwise identical conditions do not decompose to the observed products. Furthermore, formation of these products does not occur even in the presence of an organometallic compound unless accompanied by salt elimination. It is therefore not unreasonable to speculate that formation of a metal—ylide bond involving either the ylide—carbon or the ylide—oxygen is occurring.

If one could envisage subsequent formation from the metal—ylide species of the radicals RSCHR′· and RS·, the observed organic products, (RS)$_2$CHR′, (RSCHR′)$_2$ and RSSR, are exactly those expected from combination reactions of those radicals. In this regard it may be noted that unstable metal alkyls, unable to decompose by β-hydrogen transfer, frequently decompose by homolytic metal—carbon bond cleavage [7] and that reduced forms of the organometallic reactants which could have been generated by such a cleavage were frequently found among the products of the ylide reactions. Furthermore, there is evidence

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*Cp = η^5-C$_5$H$_5$; Bz = η^6-C$_6$H$_6$.

** acac = CH$_3$(CO)CHC(O)CH$_3^-$.

[5] that α-sulfinyl radicals RS(O)CHR'· which would be formed by homolytic cleavage of a metal—ylide bond, decompose in solution to the proposed radicals RS·. It may also be significant that metal—oxy species or ligand oxides were detected in some cases among the reaction products and could conceivably be arising from sulfinyl—oxygen abstraction processes leading to the proposed radicals RSCHR'·.

Whatever the mechanism, there are some less conventional organometallic products which can be obtained conveniently from reactions of this type.

Preparation of exo-[η^5-$C_6H_6CH_2S(O)Ph$]Mn(CO)$_3$

Treatment of [BzMn(CO)$_3$]ClO$_4$ with [PhS(O)CH$_2$]Li leads to formation of exo-[η^5-$C_6H_6CH_2S(O)Ph$]Mn(CO)$_3$ (Structure I).

Formation of exo-isomers has been observed previously when [BzMn(CO)$_3$]-ClO$_4$ is attacked by nucleophiles such as PhLi or NaBH$_4$ and is suggested in the present case by absence of both the exo-, C—H stretching vibration in the region 2500—2860 cm^{-1} of the product's IR spectrum and of the exo-H NMR signal, 2.4 ppm downfield from TMS [8].

## Preparation of (η^5-C_5H_5)$_2\overline{TiCH_2SC_6}H_4$

From mixtures of [PhS(O)CH$_2$]Li, [Cp$_2$TiCl]$_2$ and n-BuLi the unusual dark green compound (Structure II) was obtained.

This compound sublimes in vacuo at 130°C to give a waxy sublimate which is stable in air for several days before beginning to turn yellow. It is soluble in common organic solvents and insoluble in water. Ebullioscopic molecular weight determination in CCl$_4$ indicates that the substance is monomeric. Its mass spectrum has a molecular ion peak at $m/e = 300$ while other ions of high relative abundance are those with $m/e = 173$ and 123 corresponding to C$_{10}$H$_{10}$Ti$^+$ and PhSCH$_2^+$. The IR spectrum has only weak bands between 1030 and 1070 cm^{-1} where ν(S=O) occurs in the parent sulfoxide. There are no bands between 640 and 740 cm^{-1} but there is strong absorption at 743 cm^{-1} indicating the ortho-disubstituted nature of the phenyl ring. The NMR spectrum consists of two sharp singlets and a series of complex multiplets corresponding to the methylene, cyclopentadienyl and phenyl hydrogens, respectively.

Treatment of Cp$_2\overline{TiCH_2SC}_6H_4$ with HCl gas under dry, oxygen-free conditions produces the expected products (eq. 2).

$$Cp_2\overline{TiCH_2SC_6}H_4 + 2\,HCl \rightarrow Cp_2TiCl_2 + C_6H_5SCH_3 \tag{2}$$

(I)
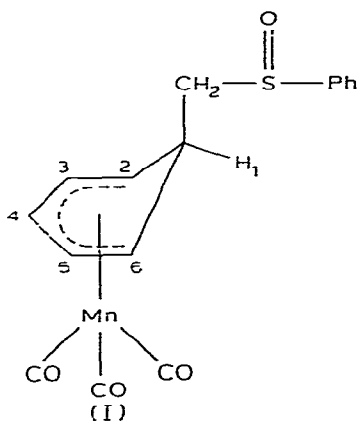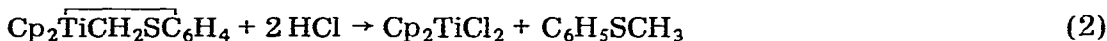
Trimethyloxonium tetrafluoroborate and methylfluorosulfonate react with $Cp_2\overline{TiCH_2SC_6H_4}$ to give the yellow *sulfonium cation* (Structure III) which can be precipitated from aqueous solution as its tetrafluoroborate salt.

(II)   (III)
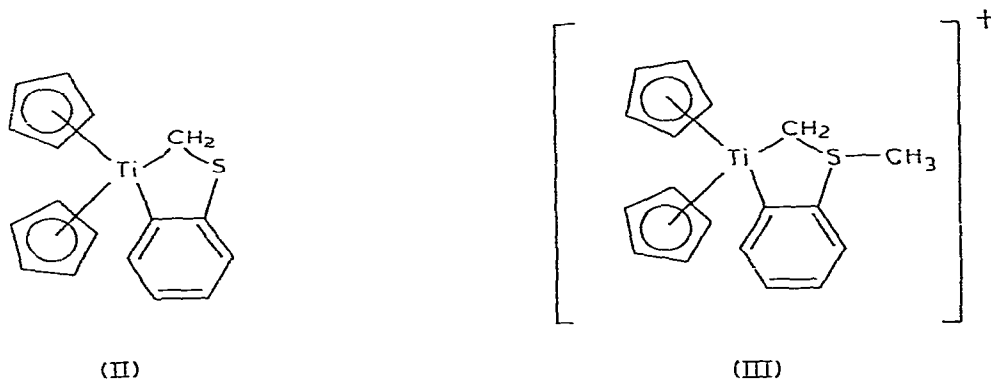
Asymmetry at sulfur in this ion causes NMR non-equivalence of the cyclopentadienyl rings which appear as two singlets and of the methylene hydrogens which appear as a quartet.

The substance $Cp_2\overline{TiCH_2SC_6H_4}$ is intensely green, reminiscent of $Cp_2TiCl \cdot L$ (L = RNH_2, R_3P) [12], $Cp_2Ti(\eta^3\text{-}C_3H_5)$ [13] or $Cp_2Ti(\eta^2\text{-}C_5H_5)$ [14] all of which are paramagnetic titanium(III) compounds. Compound II however is diamagnetic and monomeric in solution and therefore probably contains titanium(IV). Deep green colours are unusual for bis(η^5-cyclopentadienyl)titanium-(IV) systems in which two carbon atoms, other than those in the C_5 rings, are bonded to titanium. Such substances are normally yellow or orange like $(\eta^5\text{-}C_5H_5)_2\overline{TiCH_2CH_2CH_2\dot{C}H_2}$, $(\eta^5\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$ or $(\eta^5\text{-}C_5H_5)_2TiPh_2$ [15—18]. There are, however, three known examples (Structure IV) of green compounds of this type and in each case the possibility of extensive electron delocalization in the ligand exists. The example in IVc almost certainly involves delocalization, since the titanium atoms and diphenylbutadiene ligand are coplanar; a structural feature not usually found in phenyl-substituted metallocycles [19]. In the case of $Cp_2\overline{TiCH_2SC_6H_4}$ (II), methylation of the sulfur atom (III), causes a colour change from green to a more typical yellow.

(a R = R' = Ph ;
 b R = H ; R' = Ph)

(c)
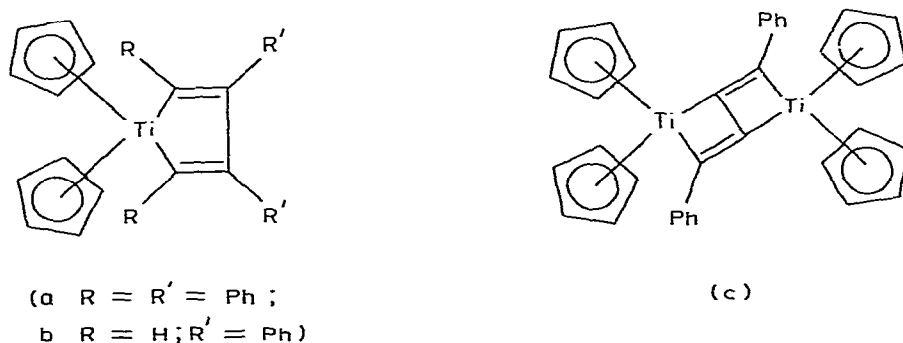
(IV)

In addition to its colour, the stability of $Cp_2\overline{TiCH_2SC_6H_4}$ is unusual. Whereas most Cp_2TiR_2 species are very sensitive to heat, light, oxygen and to attack by reagents which cleave or insert into the Ti—R bonds, $Cp_2\overline{TiCH_2SC_6H_4}$ is comparatively unreactive. Its solutions may be boiled in air for many minutes before decomposition becomes visible and the substance is stable in vacuo to at least 135°C. Passage of carbon monoxide through its benzene solutions for as long as one day causes no detectable reaction. This surprising stability may arise in several ways. Absence of β-hydrogens in the alkyl groups of Cp_2TiR_2 compounds greatly enhances stability [16]. Factors related to the compound's unusual colour may also contribute to its low reactivity and the metal is coordinatively saturated by bulky ligands, one of which is bidentate.

Unlike $Cp_2\overline{TiCH_2SC_6H_4}$, products of *ortho*-metallation typically have a donor atom such as P, S or N coordinated to the metal and bonded to a methylene group or oxygen atom which is in turn attached to the *ortho*-metallated phenyl system. No other examples of metal-bound methylene and *ortho*-metallated phenyl groups linked by a hetero-atom are known, although compounds of platinum with carbene instead of methylene—carbon are known [20].

Certain observations make it tempting to speculate on various stages in the formation of $Cp_2\overline{TiCH_2SC_6H_4}$. These stages, any one of which is likely the sum of several steps in the overall mechanism, are suggested by the following evidence and summarized in Scheme 1.
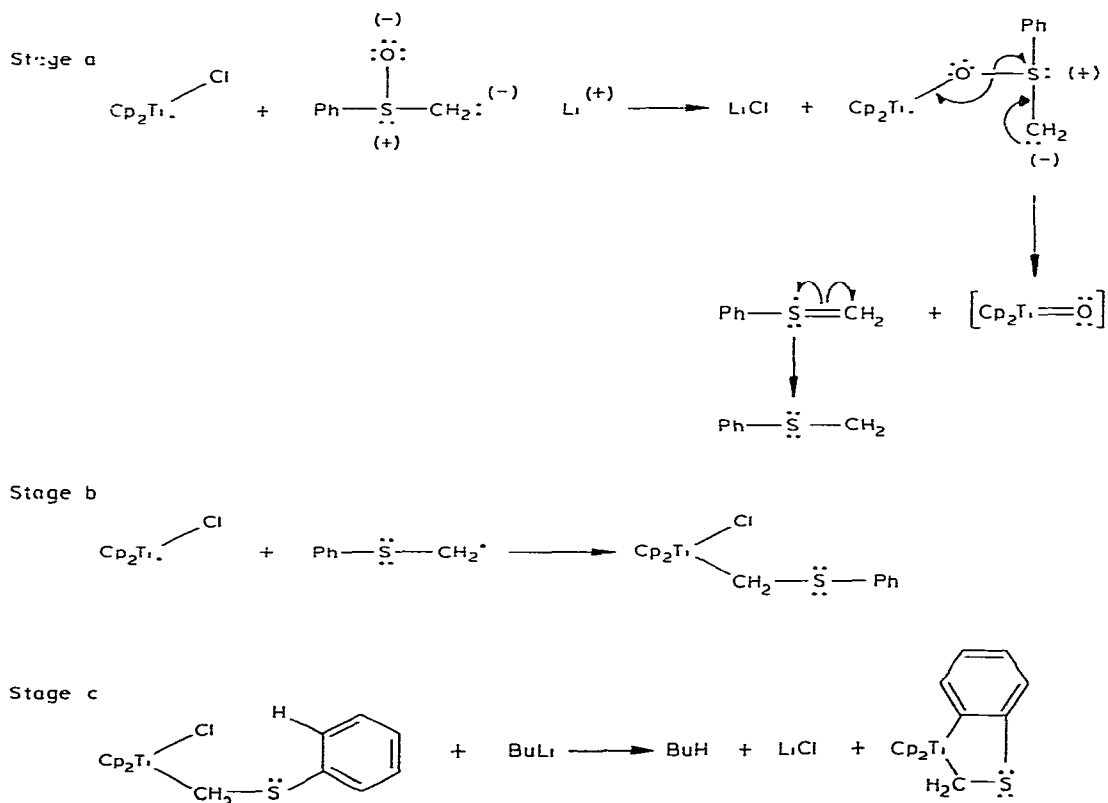
SCHEME 1

Stage a

Use of [PhSCH₂]Li instead of [PhS(O)CH₂]Li yields no metallocycle. One suspects therefore attack on titanium involves mainly sulfinyl oxygen rather than carbon. Abstraction of sulfinyl oxygen as suggested, is consistent with the well-documented ability of reduced titanium species to effect these abstractions [9—11]. Furthermore, orange, acetone-soluble cyclopentadienyl titanium-oxy species were found during work up of the reaction mixture. Organic sulfides, consistent with the presence of PhSCH₂· and PhS· were isolated from the reaction mixture.

Stage b

The stoichiometry of the process involves maximum yield of product from a reactant ratio Ti/S of 2/1. This suggests that a second mol of titanium reactant is needed in stage b, to react with some species formed in stage a in which a first mole of titanium reactant was consumed while altering the sulfur reactant. Furthermore, lowering the reaction temperature, which might be expected to prolong the lifetime of PhSCH₂· improves the yield of final product. As previously noted, use of [PhSCH₂]Li instead of [PhS(O)CH₂]Li does not yield a metallocyclic product. Therefore, attachment of the PhSCH₂ group to titanium is unlikely to involve PhSCH₂$^{(-)}$ as the attacking species. In view of previous comments concerning the possible presence of PhSCH₂· in the reaction mixture, it seems not unreasonable to propose that processes like stage b are occurring.

Stage c

This stage, which is clearly the sum of several steps, involves the abstraction of the elements of HCl by the base n-BuLi and is suggested by the fact that in the absence of n-BuLi no metallocyclic product is obtained.

Conclusions

Although of wide applicability in organic chemistry, sulfinyl carbanions seem likely to be of limited use in synthetic organometallic chemistry due to their low reactivity and to the nature of the products obtained from those reactions which do occur. In view however of an apparent tendency to generate sulfur-containing radicals in reactions with organometallic compounds, they may be useful in situations where combination of an organometallic radical and a sulfur-containing radical can lead to novel products such as Cp₂TiCH₂SC₆H₄ or to those which might otherwise be difficult to obtain.

Experimental

Starting materials were purchased or were synthesized by established methods. Sulfoxides were prepared by $NaIO_4$ oxidation of the corresponding sulfides in methanol/water at 0°C. Sulfides were prepared by coupling PhSH with RBr in alcoholic sodium ethoxide. Starting material purity was confirmed by NMR, IR and mass spectral analysis.

All procedures were carried out under anhydrous and O₂-free conditions.

Sulfinyl carbanions

Since all the ylides are thermally sensitive to varying degrees, they were prepared immediately before use.

In a typical preparation, PhS(O)CH$_2$Ph (5.8 g, 26.8 mmol) was dissolved in THF (30 ml) at 0°C and to that solution was added dropwise a 2.0 M solution in hexane of n-BuLi (13.4 ml, 26.8 mmol) with vigorous stirring at 0°C. The resulting solution of [PhS(O)CHPh]Li is light yellow.

Reactions of carbanions with organometallic reagents

The same general procedure was used for all reactions and consisted of mixing the reactants in tetrahydrofuran at −78°C. After slow warming to room temperature, volatiles were removed in vacuo and the residue extracted with pentane, ether and finally acetone or dichloromethane. Each extract was concentrated and chromatographed on Al$_2$O$_3$ to separate its components. Each component was then purified by crystallization, distillation or sublimation as appropriate to its properties and each was identified by IR, NMR, and mass spectroscopy. Procedures reported below are typical examples.

Cp$_2$TiCl$_2$

A suspension of Cp$_2$TiCl$_2$ (3.3 g, 13 mmol) in THF (250 ml) was chilled to −78°C. To this was added [PhS(O)CHPh]Li (26 mmol) in THF at −78°C. The mixture showed no apparent reaction and so was allowed to warm slowly with stirring. At −50°C the colour changed to yellow-brown and suspended solids dissolved. (The colour of this solution is stable for at least 24 h at −50°C.) Slow warming to 0°C caused appearance of a rich purple-red colour (stable at room temperature for at least 48 h). Volatiles were removed in vacuo at room temperature and the residue was extracted with pentane (3 × 125 ml). The extract was concentrated and chromatographed on Al$_2$O$_3$. Elution with hexane removed PhSCH$_2$Ph (1.5 g, 7.5 mmol) and benzene removed Cp$_2$Ti(SPh)$_2$ (0.7 g, 1.8 mmol).

The residue from pentane extraction was extracted with ether (3 × 125 ml) leaving an off-white residue of LiCl (0.1 g, 24 mmol) and TiO$_2$ (0.4 g, 5.0 mmol). The ether extracts were concentrated and chromatographed on Al$_2$O$_3$ using ether as eluant to yield (PhSCHPh)$_2$ (1.1 g, 2.8 mmol) and a further sample of Cp$_2$Ti(SPh)$_2$ (1.0 g, 2.5 mmol).

Mn(CO)$_5$Br

To a solution in THF (50 ml) of Mn(CO)$_5$Br (3.6 g, 13 mmol) was added with stirring at −78°C a suspension of [MeS(O)CH$_2$]Li (13 mmol) in THF (50 ml). The mixture was allowed to warm to room temperature and volatiles were removed in vacuo. The yellow oily residue was extracted with pentane (3 × 50 ml) and the combined extracts were concentrated and chromatographed on Al$_2$O$_3$. Pentane/ether (1/1) removed Mn$_2$(CO)$_{10}$ (0.79 g, 2.0 mmol), (MeS)$_2$ (0.10 g, 1.1 mmol) and traces of dimethylsulfoxide.

The pentane extraction residue was extracted again with ether (3 × 100 ml) leaving an off-white residue of LiBr (1.1 g, 12.8 mmol). Chromatography of the concentrated extracts on alumina gave Mn$_2$(CO)$_{10}$ (1.3 g, 3.3 mmol), (MeS)$_2$ (0.13 g, 1.4 mmol) and MeS(O)Me (0.52 g, 6.7 mmol).

(Et₃P)₂NiCl₂

(Et$_3$P)$_2$NiCl$_2$

To a solution in THF (100 ml) of (Et$_3$P)$_2$NiCl$_2$ (3.6 g, 10 mmol) was added with stirring at $-78°$C a solution of [PhS(O)CHPh]Li (20 mmol) in THF (100 ml). The mixture was allowed to warm to room temperature and volatiles were removed in vacuo. The red-brown tarry residue was extracted with pentane (3 × 100 ml) and with ether (3 × 100 ml) leaving a light brown powdery residue which was extracted with CH$_2$Cl$_2$ (3 × 100 ml) to leave an off-white residue of LiCl (0.69 g, 16 mmol). The brown powder could not be recovered from CH$_2$Cl$_2$ either by crystallization or by removal of the solvent. It was unstable in air and during chromatography of its solution. It was not identified.

The extracts were concentrated and chromatographed on Al$_2$O$_3$. Elution of the pentane extract with 30/70 benzene/pentane gave Et$_3$P (1.5 g, 13 mmol) and Et$_3$PO (0.16 g, 1.2 mmol) as a mixture. They were separated by vacuum distillation in a short path distillation apparatus with the Et$_3$PO crystallizing on the water-cooled probe. Further elution of the pentane extract using benzene eluant gave PhS(O)CH$_2$Ph (0.86 g, 4.0 mmol), (PhS)$_2$ (0.26 g, 1.2 mmol), (PhS)$_2$CHPh (0.46 g, 1.5 mmol) and (PhSCHPh)$_2$ (0.24 g, 0.6 mmol). Chromatography of the ether extract using ether eluant gave more (PhS)$_2$ (trace), (PhSCHPh)$_2$ (0.72 g, 1.8 mmol) and (PhS)$_2$CHPh (0.18 g, 0.6 mmol).

Other reactions

Yields are based on metal, sulfur or phosphorus, as appropriate.

(i) of [MeS(O)CH₂]Li. (a) with: CpFe(CO)$_2$Cl; product (yield): LiCl (92), [CpFe(CO)$_2$]$_2$ (55), (MeS)$_2$ (21), (MeSCH$_2$)$_2$ (8), MeSH (detected spectroscopically).

(b) with: Cp$_2$VCl$_2$; product (yield): LiCl (86), (MeS)$_2$ (13), (MeSCH$_2$)$_2$ (11), MeSH (detected spectroscopically), MeS(O)Me (48), no tractable vanadium product.

(c) with: Cp$_2$TiCl$_2$; products (yield): LiCl (89), Cp$_2$Ti(SMe)$_2$ (31), (MeS)$_2$ (9), MeSH (detected spectroscopically), TiO$_2$ (43).

(ii) of [PhS(O)CH₂]Li. (a) with: CpFe(CO)$_2$Cl; product (yield): LiCl (92), [CpFe(CO)$_2$]$_2$ (51), (PhS)$_2$ (29), (PhSCH$_2$)$_2$ (10), (PhS)$_2$CH$_2$ (22).

(b) with: CpFe(CO)[P(OPh)$_3$]Cl; product (yield): LiCl (95), [CpFe(CO)$_2$]$_2$ (43), (PhS)$_2$ (30), (PhSCH$_2$)$_2$ (25), (PhS)$_2$CH$_2$ (31), P(OPh)$_3$ (65).

(c) with: CpFe[P(OPh)$_3$]$_2$Cl; product (yield): LiCl (98), Cp$_2$Fe (27), (PhS)$_2$ (25), (PhSCH$_2$)$_2$ (38), (PhS)$_2$CH$_2$ (27), P(OPh)$_3$ (73).

(d) with: Cp$_2$VCl$_2$; product (yield): LiCl (79), (PhS)$_2$ (10), (PhSCH$_2$)$_2$ (6), (PhS)$_2$CH$_2$ (8), PhS(O)CH$_3$ (63), no tractable vanadium product.

(e) with: Cu[CH$_3$C(O)CHC(O)CH$_3$]$_2$; product (yield): Li[CH$_3$C(O)CHC(O)-CH$_3$] (54), (PhS)$_2$ (21), (PhSCH$_2$)$_2$ (10), (PhS)$_2$CH$_2$ (13), PhS(O)CH$_3$ (41), no tractable copper-containing product.

(f) with: (Et$_3$P)$_2$NiCl$_2$; product (yield): LiCl (88), (PhS)$_2$ (9), (PhSCH$_2$)$_2$ (31), (PhS)$_2$CH$_2$ (21), Et$_3$P (53), Et$_3$PO (11), PhS(O)CH$_3$ (26), no tractable nickel product.

(g) with: Cp$_2$TiCl$_2$; product (yield): LiCl (92), Cp$_2$Ti(SPh)$_2$ (28), (PhS)$_2$ (2), (PhS)$_2$CH$_2$ (29), TiO$_2$ (44).

(h) with: Mn(CO)$_5$Br; products (yield): LiBr (93), Mn$_2$(CO)$_{10}$ (87), (PhS)$_2$ (40), PhS(O)Me (41).

(i) with: $[CpFe(CO)_2PPh_3]Cl$; products (yield): LiCl (94), $[CpFe(CO)_2]_2$ (63), $(PhS)_2$ (31), $(PhSCH_2)_2$ (27), $(PhS)_2CH_2$ (33), Ph_3P (67), Ph_3PO (17).

(iii) of [PhS(O)CHPh]Li. (a) with: $CpFe[P(OPh)_3]_2Cl$; product (yield): LiCl (88), Cp_2Fe (12), $(PhS)_2$ (19), $(PhSCHPh)_2$ (44), $(PhS)_2CHPh$ (9), $P(OPh)_3$ (50).

(b) with: $[CpFe(CO)_2PPh_3]Cl$; product (yield): LiCl (91), $[CpFe(CO)_2]_2$ (52), $(PhS)_2$ (22), $(PhSCHPh)_2$ (25), $(PhS)_2CHPh$ (36), Ph_3P (58), Ph_3PO (5).

(a) Preparation of $Cp_2\overline{TiCH_2SC_6H_4}$

A dark green solution of $[Cp_2TiCl]_2$ was prepared by suspending Cp_2TiCl_2 (1.7 g, 7.0 mmol) in THF (50 ml) and stirring for two hours with 5% sodium amalgam containing 0.16 g (7.0 mmol) of Na. The solution was allowed to settle for two hours and then decanted from the mercury and finely divided precipitate, before being chilled to $-78°$C.

A separate solution of PhS(O)Me (0.5 g, 3.5 mmol) was prepared in THF (50 ml) and cooled to $0°$C. To the cooled solution was added dropwise with stirring a 2.0 M solution of n-BuLi in hexane (3.5 ml, 7.0 mmol). This yellow solution was chilled to $-78°$C and added with stirring to the green solution of $[Cp_2TiCl]_2$. No apparent colour change occurred. The mixture was warmed to room temperature and filtered to give an off-white residue of LiCl (0.25 g, 5.9 mmol). Volatiles were removed in vacuo and the dark green residue was extracted with benzene (3 X 50 ml) leaving an orange residue which has IR absorptions (Nujol mull) at 3080, 1010 and 810 cm^{-1} (due to η^5-Cp) and 720 cm^{-1} (typical of Ti—O). This substance has an NMR spectrum in acetone-d_6 consisting of a single peak at τ = 3.75. It was not characterized further.

The green extracts were concentrated and chromatographed on an Al_2O_3 column using 4/1, hexane/benzene as eluant. A mixture of $\overline{PhSCH_2SPh}$ and PhSSPh was eluted followed by a green band of $Cp_2\overline{TiCH_2SC_6H_4}$. The green product can be purified by sublimation at $130°$C and 0.1 mmHg although this is accompanied by substantial decomposition to purple-red $Cp_2Ti(SPh)_2$. Yield: 0.33 g, or 31% based on sulfur. Ebullioscopic molecular weight in CCl_4 265; required 300. Mass spectrum parent ion peak at m/e = 300. NMR at 60 MHz in acetone-d_6 or $CDCl_3$ shows little solvent dependence. In ppm from internal TMS: 7.2 (m) (1H, Ph), 6.6 (m) (2H, Ph), 6.5 (m) (1H, Ph), 6.20 (s) (10H, Cp), 2.16 (s) (2H, CH_2). Analysis. Found: C, 67.85; H, 5.43; S, 10.91; Ti, 15.23. $C_{17}H_{16}STi$ calcd.: C, 68.00; H, 5.37; S, 10.68: Ti, 15.95%.

When prepared at room temperature, the yield of green product is decreased to 17% and 0.50 g of TiO_2 (9%) is also obtained.

(b) $[Cp_2\overline{TiCH_2S(Me)}C_6H_4]BF_4$

A solution of $Cp_2\overline{TiCH_2SC_6H_4}$ (0.5 g, 1.7 mmol) in 1/1 benzene/hexane was treated with an equimolar amount of $MeOSO_2F$ at room temperature. After stirring for 5 min, the solution was pale yellow and a yellow precipitate had formed which was separated and washed with ether and then dried. The solid was dissolved in water (200 ml) and an aqueous solution of NH_4BF_4 added dropwise until formation of a yellow oil ceased. The mixture was centrifuged and the aqueous supernatant decanted. The oil was washed with water (2 X 50 ml), dried in vacuo overnight and then recrystallized from acetone. NMR at 60 MHz in acetone-d_6 in ppm from internal TMS: 7.89 (m) (1 H, Ph), 7.58 (m)

(1 H, Ph), 6.98 (m) (2H, Ph), 6.73 (s) (5H, Cp), 6.59 (s) (5H, Cp), 3.83 (q, J(AB) 11 Hz) (2H, CH$_2$), 3.05 (s) (3H, Me). IR is very similar to that of $\overline{Cp_2TiCH_2SC_6H_4}$ except for a very strong broad absorption at 1050 cm^{-1} (BF$_4^-$). Analysis. Found: C, 54.37; H, 4.70. C$_{18}$H$_{19}$BF$_4$STi calcd.: C, 53.76; H, 4.76%.

(c) Reaction of $\overline{Cp_2TiCH_2SC_6H_4}$ with HCl

Green $\overline{Cp_2TiCH_2SC_6H_4}$ (0.3 g, 1 mmol) was dissolved in dry de-gassed THF (50 ml) at room temperature. Dry HCl gas was bubbled through the solution for two minutes during which time the solution turned red-brown. Volatiles were removed in vacuo and the oily residue was heated at 0.1 mmHg to 130°C in a short path distillation apparatus. From the water cooled probe was collected PhSMe (0.1 g, 0.8 mmol). The residue was washed with pentane (5 ml) and ether (5 ml) leaving red Cp$_2$TiCl$_2$ (0.2 g, 0.8 mmol).

[η^5-C$_6$H$_6$CH$_2$S(O)Ph]Mn(CO)$_3$

A suspension of [BzMn(CO)$_3$]ClO$_4$ (1.6 g, 5.0 mmol) in THF (75 ml) was treated at −78°C with a THF solution of [PhS(O)CH$_2$]Li (5.0 mmol). An immediate reaction occurred giving a dark yellow-brown solution which was warmed to room temperature with stirring and then filtered. Volatiles were removed in vacuo leaving a viscous brown oil which was placed on an Al$_2$O$_3$ column and eluted with 2/1 ether/hexane. This removed a yellow band of Mn$_2$(CO)$_{10}$ and further elution with 2/1 CH$_2$Cl$_2$/ether removed a very viscous yellow-brown oil which crystallized slowly to give mainly yellow crystals and a few red tabular ones. The red crystals which were not identified but appear to be paramagnetic from their NMR characteristics were removed by hand. The yellow crystals of [η^5-C$_6$H$_6$CH$_2$S(O)Ph]Mn(CO)$_3$ appear to contain trace amounts of a paramagnetic impurity causing broadening of NMR signals in all samples except those purified by sublimation at 125°C and 0.1 mmHg. Sublimation gives analytically pure material but is accompanied by substantial decomposition.

The yellow product was recrystallized from acetone. It is insoluble in benzene, hexane and CCl$_4$ and dissolves but reacts slowly in CHCl$_3$ and CH$_2$Cl$_2$. Yield 1.1 g or 62%. The mass spectrum has a parent ion peak at m/e = 356 (calcd. mol. wt. 356).
Analysis. Found: C, 53.68; H, 4.01; S, 9.23; Mn, 15.11. C$_{16}$H$_{13}$MnO$_4$S calcd.: C, 53.94; H, 3.68; S, 9.00; Mn, 15.42%.
NMR in acetone-d_6 at 60 MHz in ppm from internal TMS: 7.51 (m) (5H, Ph), 5.98 (t of t, J 5 and 1 Hz) (1H, H$_4$), 4.99 (t, J 6 Hz) (2H, H$_3$ and H$_5$), 3.14 (m) (3H, H$_1$ + H$_2$ + H$_6$) 2.68 (m, $J \sim$ 4 Hz) (2H, CH$_2$).

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