Thiolate and Thioether Functions as Donor Groups X, Y in Tripod Ligands $RCH_2C(CH_2PPh_2)(CH_2X)(CH_2Y)$ – Synthesis and Coordination Chemistry☆

Rainer Soltek and Gottfried Huttner*

Anorganisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany
Fax: (internat.) + 49(0)6221/545707

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Tripod ligands $RCH_2C(CH_2PPh_2)(CH_2X)(CH_2Y)$ (**1**) with X, Y = SAlkyl, SBzl selectively undergo reductive cleavage of the SBzl function with Li/NH_3/THF at –40 °C to produce $RCH_2C(CH_2PPh_2)(CH_2X)(CH_2Y)$ (**2**) (X, Y = SAlkyl, SH). In these mixed donor set ligands the SH functions are the least coordinative ones such that $[\eta^2$-$\{CH_3C(CH_2PPh_2)(CH_2SEt)$-$(CH_2SH)\}(CO)_4Mo]$ (**5**) is a stable compound with an uncoordinated SH function at the dangling arm of the ligand. If the SH functions of a potential tripod ligand are deprotonated the resulting thiolate functions are found to strongly coordinate in compounds such as $[\eta^3$-$\{CH_3C(CH_2PPh_2)_2(CH_2S)\}(CO)_3Mo]^-$ which are obtained as their lithium and sodium salts **6**. These highly reactive species may be stabilized by encapsulating their alkali counter ions in cryptands and the corresponding salts with [2,1,1]cryptand (**7a**) and [2,2,2]cryptand (**7b**) are far easier to handle than the cryptand-free progeners **6**. Alkylation of the coordinatively bound thiolate function in **6** leads to the corresponding thioether derivatives $[\eta^3$-$\{CH_3C(CH_2PPh_2)_2$-$(CH_2SR)\}(CO)_3Mo]$ (**8**).

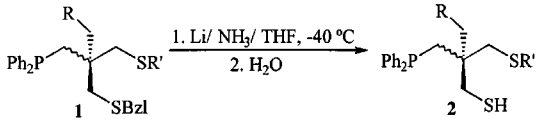
Introduction

The coordination chemistry of tripod ligands $CH_3C(CH_2PPh_2)_3$ developed by L. Sacconi and his school has quite some unconventional features which show that the η^3 coordination of a neopentane-based tripod ligand is able to induce a reactive potential at the metal center which is otherwise not accessible[1][2]. The potential of this type of ligand should be greatly enhanced by an appropriate variation of the donor functions and in fact there is a promising chemistry with ligands of type $RC(CH_2X)_3$ containing donor functions X other than PPh_2[2][3][4]. A still broader scope of this chemistry could be envisaged if it were possible to synthesize ligands $CH_3C(CH_2X)(CH_2Y)(CH_2Z)$ with up to three different phosphorus donor groups. The difficulties characterizing the neopentane chemistry, which is at the basis of such syntheses, had only recently been overcome and neopentane-based tripod ligands with up to three different phosphorus donors have been described[5][6][7][8][9][10][11][12][13] with even enantioselective syntheses of such ligands having been reported[10]. The introduction of sulfur and nitrogen donors instead of phosphorus donor functions in this type of tripod ligand has by now not yet found a general solution. Even though different strategies for introducing these types of donor functions have been worked out for special cases[14][15][16][17][18]. It is shown in this paper how tripod ligands containing one or more thioether or thiolate donor functions may be obtained and how these molecules behave as ligands in their $[(CO)_3Mo]$ and $[(CO)_4Mo]$ derivatives.

Results and Discussion

Preparation of the Ligands

There are two main pathways to obtain tripod ligands containing thiole functions, one of them being the nucleophilic cleavage of thietanes by phosphides[15][16] and the other one relying upon the reductive cleavage of SBzl groups by lithium[15].



1	R	R′	**2**	R	R′
1a	H	Et	**2a**	H	Et
1b	H	*i*Pr	**2b**	H	*i*Pr
1c	H	Bzl	**2c**	H	H
1d	CH_3O	Bzl	**2d**	CH_3O	H

This second method was used to transform compounds **1**[18][19], containing at least one SBzl group into tripod ligands containing thiole functions (**2**).

Starting from compounds **1**[18][19] applying the "lithium reduction step"[15] to **1**, followed by hydrolytic workup gives the thiole tripod ligands **2**. **2a** and **2b**, containing one thiole function, are obtainted as colorless oils while **2c** and **2d**, bearing two thiole functions, are colorless microcrystalline solids. Their identity is proven by NMR and mass spectra

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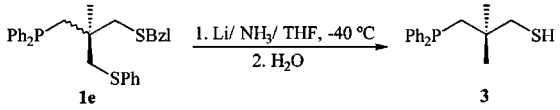
Table 1. ^{1}H-NMR data

^{1}H NMR[x] X,Y	CH_2P	CH_2X	CH_2Y	X	Y	CH_3C_q or CH_3OCH_2	aromat. H	cryptand
2a	2.36, d,	2.73,	2.72−2.67, m, 2 H	2.50, q, 2 H, 7.3[b]	1.29−1.24,	1.05, s,	7.55−7.32,	−
SEt, SH	2 H, 3.7[a]	s, 2 H		1.24, t, 3 H, 7.3[b]	m, 1 H	3 H	m, 10 H	
2b	2.35, d,	2.70,	2.67, d,	2.80, spt, 1 H, 6.6[b]	1.28−1.22,	1.03, s,	7.55−7.32,	−
*Si*Pr, SH	2 H, 3.3[a]	s, 2 H	2 H, 10.2[b]	1.28−1.22, m, 6H	m, 1 H	3 H	m, 10 H	
2c	2.34, d,	2.70, d,		1.16, t,		1.04, s,	7.51−7.28,	−
SH, SH	2 H, 3.7[a]	4 H, 8.8[b]		2 H, 9.0[b]		3H	m, 10 H	
2d	2.35, d,	2.75, d,		1.17, t,		3.27, s, 2H	7.56−7.35,	−
SH, SH,	2 H, 3.8[a]	4 H, 9.0[b]		2 H, 9.0[b]		3.10, s, 3H	m, 10 H	
3	2.35, d,	2.67, d,	−	1.25, t,	−	1.10, s,	7.57−7.39,	−
SH, −	2 H, 3.2[a]	2 H, 8.8[b]		1 H, 8.8[b]		6H	m, 10 H	
5	2.59, d,	2.93, 2.76,	2.48, 2.29, 2dd,	2.86, q, 2 H, 7.3[b]	1.17, t,	0.93, bs,	7.68−7.43,	−
SEt, SH	2 H, 7.6[a]	2d, 2 H, 7.3[b]	2 H, 13.9[c], 9.0[b]	1.45, t, 3 H, 7.3[b]	1 H, 9.0[b]	3H	m, 10 H	
6a	2.30, 2.05, 2dd,		2.14, s, 2 H	−	−	1.14, bs,	8.10−7.28,	−
PPh_2, S	4 H, 14.4[c], 7.4[a]					3H	m, 20 H	
6b	2.22, 1.94, 2dd,		2.05, s, 2 H	−	−	0.98, bs,	7.95−7.00,	−
PPh_2, S	4 H, 14.2[c], 6.6[a]					3H	m, 20 H	
6c	2.22, d,	2.35, 2.21, 2d,		−	−	2.78, s, 2H	8.10−7.28,	−
S, S	2 H, 9.0[a]	4 H, 12.8[c]	2.13, s, 2 H			3.13, s, 3H	m, 10 H	
7a		2.39, 2.05, 2dd,		−	−	1.14, bs,	8.09−7.21,	3.72−3.60, m, 20 H
PPh_2, S		4 H, 14.4[c], 7.2[a]	1.77, s, 2 H			3H	m, 20 H	2.95−2.60, m, 12 H
7b		2.05, 1.81, 2dd,		−	−	0.76, bs,	7.86−6.88,	3.44, 3.39, 2s, 24 H
PPh_2, S		4 H, 14.0[c], 7.0[a]	2.40, s, 2 H			3H	m, 20 H	2.46, bs, 12 H
8a		2.35, d,		−	2.18,	1.33, t,	7.77−7.12,	−
PPh_2, SMe		2 H, 6.2[a]	2.46, s, 2 H		s, 3H	3 H, 2.2[d]	m, 20 H	
8b		2.39−2.32,		−	2.40, q, 2 H, 7.3[b]	1.33, t,	7.76−7.05,	−
PPh_2, SEt		m, 4H	2.15, s, 2 H		1.18, t, 3 H, 7.3[b]	3 H, 2.5[d]	m, 20 H	
8c		2.37, 2.27, 2dd,		−	3.54,	1.23, t,	7.76−7.01,	−
PPh_2, SBzl		4 H, 15.3[c], 5.7[a]			s, 2 H	3 H, 2.5[d]	m, 25 H	

[x] **2** and **3** in $CDCl_3$, **5** and **8** in CD_2Cl_2, **6** in [D_8]THF, **7** in CD_3CN. − [a] $^2J_{HP}$. − [b] $^3J_{HH}$. − [c] $^2J_{HH}$. − [d] $^4J_{HP}$.

as well as by elemental analyses (Tables 1 and 2, Experimental Section). Judging from the variety of groups present in the starting compounds **1** the scope and selectivity of the applied method − i.e. generating thiole functions in tripod ligands by the reductive cleavage of SBzl functions − are quite broad. A limitation is, however, met when an SPh and an SBzl function are both present in **1**.



In this case the CH_2SPh group is cleaved at the CH_2S bond as is shown by the transformation of **1e** to **3** (Experimental Section, Tables 1 and 2).

Coordination Chemistry

The coordination chemistry of tripod ligands containing thiole functions has not been worked out in much detail. There are some compounds derived from such ligands with manganese[14] or nickel[15] as the coordinated metals; in each of these cases, however, the thiole function had been transformed into a thiolate functionality during the process of coordination. The coordination of RSH functions themselves is not too common even if they are not part of a tripod ligand[20]. Although even the coordination of H_2S as a two-electron donor has been observed[21] the reaction of RSH with coordinatively unsaturated ligand-metal entities appears to be hampered with difficulties. It has been found that the reaction of [$Cp(CO)_2MnTHF$], which in itself is a precursor of the 16-electron [$Cp(CO)_2Mn$] fragment, with RSH leads to the formation of the radical compunds [$Cp(CO)_2MnSR$] with a concommitant hydrogen abstraction of the thiole function[22]. It is not astonishing therefore that the reaction of $CH_3C(CH_2PPh_2)_2CH_2SH$ (**4**)[15] with [$(MeCN)_3(CO)_3Mo$] in CH_2Cl_2 does not result in isolabable and well-charcterizable tripod compounds of the hypothetical formula [η^3-{$CH_3C(CH_2PPh_2)_2CH_2S$}$(CO)_3Mo$]. Instead a yellow to brownish solution of what is obviously a mixture of compounds is obtained. Trying to isolate a definite compound from this mixture by transforming any SH functions into thiolate groups by NaH or *n*BuLi leads to a brownish product from which, however, no definite compounds could be isolated even after addition of crown ethers or cryptands as potential precipitating agents (see, however, the preparation of **7**, below).The yellow to brownish solutions which result from the deprotonation step (see above) are highly sensitive to air. They immediately change color at the first contact with a trace of oxygen to give deep blue solutions.

While the deep color reminds of the radical compounds [$Cp(CO)_2MnSR$][22] no definite product could be isolated either and the blue powders which remain after evaporation

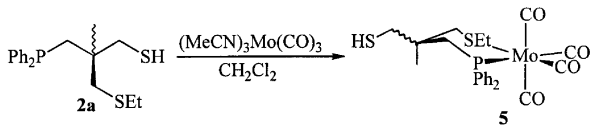
Table 2. ^{13}C-NMR data

^{13}C NMR[x] X, Y	CH_2P	CH_2X	CH_2Y	X	Y	CH_3C_q CH_3OCH_2	orCH_3C_q	aromat. C	CO/ cryptand
2a SEt, SH	38.2, d, 16.5[a]	42.2, d, 9.6[b]	34.7, d, 10.1[b] 34.8, d,	27.5, s 14.8, s	–	24.8, d, 9.6[b]	39.0, d, 13.8[c]	139.2–128.1, m	–
2b S*i*Pr, SH	38.4, d, 16.5[a]	40.6, d, 9.6[b]	9.7[b] 33.9, d, 11.0[b]	36.2, s 23.4, s	–	24.9, d, 9.2[b]	38.8, d, 13.8[c]	139.1–128.0, m	–
2c SH, SH	37.1, d, 16.5[a]		30.0, d, 10.9[b] –	–	–	24.0, d, 9.2[b]	38.7, d, 12.9[c]	139.0–128.3, m	–
2b SH, SH	33.2, d, 16.8[a]		48.2, d, 6.0[b]	–	–	74.6, d, 8.7[b] 59.1, s	43.4, d, 12.3[c]	142.3–126.4, m	–
3 SH, –	40.9, d, 16.4[a]	38.4, d, 10.4[b] 37.7, d,	–	–	–	28.3, d, 9.1[b]	35.8, d, 13.3[c]	140.3–128.9, m	–
5 SEt, SH	38.7, d, 13.1[a]	6.7[b] 32.7, t,	–	38.6, d, 5.6[b] 13.7, s	–	27.4, d, 6.0[b]	39.1, d, 2.5[c]	138.2–128.8, m	[d]
6a PPh_2, S	36.5, pt, 8.5[a][b]	5.5[b] 34.9,	–	–	35.9, t, 9.0[b]	39.1, t, 4.4[c]	143.4–127.3, m	223.7, t, 8.7[c]; 223.0, dd, 41.0[e], 14.0[f]	
6b PPh_2, S	38.5, pt, 8.5[a][b]	bs	–	–	36.0, t, 8.4[b]	37.7, t, 4.4[c]	143.5–127.3, m	226.1–224.9, m	
7a PPh_2, S	37.9–34.8, m	43.9, t,	–	–	37.9–34.8, m		143.2–127.7, m	[d]; 68.96, 67.66, 65.92, 3s[g] 51.79, 50.51, 2s[h]	
7b PPh_2, S	37.9–34.9, m	4.6[b] 41.6, t,	–	–	37.9–34.9, m	37.7, t, 5.5[c]	143.2–127.8, m	[d]; 68.59, 67.71, 2s[g] 52.62, s[h]	
8a PPh_2, SMe	36.0, pt, 7.4[a][b]	4.6[b] 38.3, t,	–	27.7, t, 5.5[b]	37.7, t, 9.2[b]	38.2– 38.0, m	139.9–128.6, m	220.8, m	
8b PPh_2, SEt	36.8, pt, 8.5[a][b]	4.4[b]		38.2–38.0, m 13.7, s	37.5, t, 8.7[b]	37.6– 6.3, m	141.5–128.4, m	[d]	
8c PPh_2, SBzl	37.6–36.3, m			47.2, t, 5.1[b]	35.1, t, 8.3[b]		139.8–127.0, m	222.5–219.0, m	

[x] **2** and **3** in $CDCl_3$, **5** and **8** in CD_2Cl_2, **6** in [D_8]THF, **7** in CD_3CN – [a] $^1J_{CP}$. – [b] $^3J_{CP}$. – [c] $^2J_{CP}$. – [d] Due to worse solubility no ^{13}CO resonances observed. – [e] $^2J_{CPtrans}$. – [f] $^2J_{CPcis}$. – [g] CH_2O. – [h] CH_2N.

of the solvent give only very weak EPR signals and are not highly paramagnetic as would be expected for radical species when analyzed on a magnetic balance. Chromatography of the blue solutions on silica gel is of no help since the blue phase rather rapidly desintegrates during the process of elution. The nature of the compounds and intermediates obtained from **4** by the above procedure does remain unknown (see, however, the transformation of **4** to **7**, below).

In contrast to the reaction of **4** with $[(MeCN)_3(CO)_3Mo]$ the ligand **2a** reacts with the same reagent to produce the $(CO)_4Mo$ derivative **5** in fair yields.



The formation of $(CO)_4Mo$ derivatives from $[(MeCN)_3(CO)_3Mo]$ is not an uncommon observation[17]. Even though no single crystals suitable for an X-ray analysis could be obtained from **5** its constitution as given is clear from spectroscopic data.

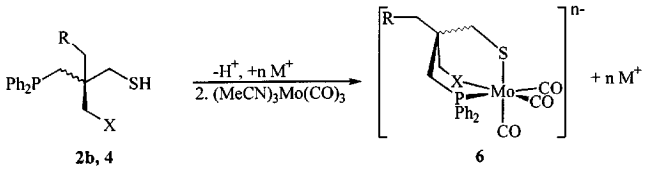
The $\tilde{\nu}_{CO}$ spectrum is characteristic for a $[(CO)_4Mo]$ entity[23]. The coordination of the phosphorus function is evident from its ^{31}P-NMR resonance which is found at δ = 20.0 in constrast to the chemical shift of the free ligand (δ = –26.9). The coordination of the SEt group is evidenced by a $^3J_{CP}$ coupling of 5.6 Hz to the α-carbon atom of the ethyl group (Table 2). There is no such coupling to the proton of the SH group of the dangling arm with the ^{1}H-NMR signal

Table 3. Infrared data of **5–8**

	Solvent	$\tilde{\nu}_{CO}$ [cm^{-1}]		
5	CH_2Cl_2	2020 (s)	1901 (s, br.)	1870 (s)
6a	THF	1911 (s)	1816 (s)	1787 (s)
6b	THF	1909 (s)	1815 (s)	1779 (s)
6c	THF	1885 (s)	1771 (s)	1718 (s)
7a	MeCN	1905 (s)	1809 (s)	1778 (s)
7b	MeCN	1909 (s)	1802 (s)	1763 (s)
8a	CH_2Cl_2	1927 (s)	1830 (s)	1795 (s)
8b	CH_2Cl_2	1929 (s)	1837 (s)	1811 (s)
8c	CH_2Cl_2	1934 (s)	1844 (s, br.)	

referring to this group being a clear-cut triplet as expected (Table 1). The CH_2 protons of the dangling arm are diastereotopic which, together with a coupling to the SH proton, results in a pattern of two doublets of doublets. ^{31}P decoupling substanciates the assignments. With correct mass spectra and elemental analyses the identity of **5** as shown is beyond doubt therefore.

The observation that in **5** the thiole function cannot compete with the donors present in the reaction solution suggests a different strategy: if the thiole function of the ligand is deprotonated the thiolate function thus formed should have better ligand capabilities such that tripodal coordination of the anionic ligands might ensue. If salts of these derivatives could be isolated protonation of the coordinated thiolate functions might well lead to coordinated SH functions in tripodal metal compounds.



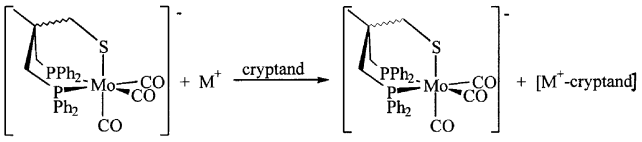
2b, 4 **6**

	R	X	**6**	R	X	M	*n*
4	H	PPh_2	**6a**	H	PPh_2	Li	1
2d	CH_3O	SH	**6b**	H	PPh_2	Na	1
			6c	CH_3O	S	Na	2

If the ligand **4** is deprotonated by *n*BuLi in THF and the resulting solution is treated with $[(MeCN)_3(CO)_3Mo]$ the lithium salt **6a** results, in which all three donor functions of the tripod ligand are engaged in coordination. **6a** is isolated from the reaction solution as its adduct with two molecules THF per unit by evaporating the solvent and washing the brown oily residue with petroleum ether in an ultrasonic bath. The product as isolated is very sensitive to oxygen and moisture so that its yellow solutions turn first green and finally blue under atmospheric conditions. Under unaerobic conditions the solutions are stable enough to warrant detailed analyses by NMR. The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra are in accord with the formula as given (Tables 1 and 2). The coordination of both phosphorus centers is apparent from the appearance of one single signal at $\delta = 21.6$. The coordination of the sulfide function is not definitely established by $^3J_{CP}$ coupling constants between the phosphorus nucleus and the methylene carbon atom to which the sulfur atom is bound, since $^3J_{CP}$ coupling through the ligand framework gives rise to values of similar magnitude[15]. From the three CH_2 groups of the chelate cage the one linked to the sulfur atom has two chemically equivalent hydrogen atoms and a singlet is observed for this group in the ^{1}H-NMR spectrum. The hydrogen atoms at the CH_2 groups linked to the phosphorus atoms are diastereotopic and give rise to two doublets of doublets (Table 1). The symmetry of **6a** is thus clearly reflected by its ^{1}H-NMR spectrum. The tridentate binding mode of the ligand on the other hand is not a necessary prerequisit to explain the spectra. Since **6a** contains two THF solvate molecules per formula unit (the ratio of THF/**6** is determined by integration of the $[H_8]$THF signals apparent for solutions of the compounds in isotopically pure $[D_8]$THF) it might be argued that the ligand is only acting in the bidentate fashion with one THF molecule occupying the vacant coordination site at the metal. Even the observation of a $\tilde{\nu}_{CO}$ IR pattern which corresponds to a $[(CO)_3Mo]$ entity (Table 3) does not differentiate between the two possibilities. An indication that the constitution of **6** as shown might be correct may be found in the values of the chemical shifts of the carbonyl carbon atoms of **6**. The two different classes of carbonyl groups (*trans* to P, *trans* to S) have their resonances in close vicinity which is well expected if the sulfur and phosphorus atoms act as the *trans* ligand but would not be easily explained if THF and P were in the corresponding positions. The pattern of the $^2J_{CP}$ coupling constants (Table 2) is in accord with an overall octahedral geometry of the compound. One argument in favor of the η^3 coordination of the ligand in **6a** comes from a comparison of the ^{13}C-NMR resonances observed for compounds which definitely contain the ligands in η^2 coordination (e.g. **5**) and a series of examples in ref.[18] where it was found that the relevant resonances of **6a** occur at different shift values which are much closer to the values characterictic for compounds with η^3 coordination (**8**) and a series of compounds in ref.[18]. Yet a stronger argument comes from the observation that the solvent-free salt obtained from **6a** by the addition of [2,1,1]cryptand (**7a**, see below) have their NMR resonances at approximately the same values as observed for **6a** (Tables 1 and 2).

Observations very similar to the results reported for **6a** are made for its sodium analogue **6b** which results when NaH is used as the deprotonating agent in the transformation of **4** to **6** (Tables 1−3). With **2d** as the starting material **6c** is formed under these conditions. **6b** as well as **6c**, when isolated as yellow powders following the workup procedure described for the synthesis of **6a**, are both found to contain two THF molecules per formula unit. The chemical shifts observed for the constitution of the compounds in the various NMR spectra are close to the ones reported for **6a** (Tables 1−3). In contrast to the situation in **6a**, instead of the protons at the CH_2S group now the protons at the CH_2P entity are chemically equivalent with the remaining two CH_2S groups showing the phenomenon of diastereotopicity in the case of **6c**. This symmetry property is clearly evident from the ^{1}H-NMR spectrum (Table 1).

Compounds **6** are rather difficult to handle due to their high sensitivity to oxygen and moisture as well as to the fact that the only solvent in which comparatively stable solutions are formed is THF while solvents with higher proton activity and/or oxidation power (e.g. CH_3CN, CH_3NO_2) lead to desintegration of the compounds.



6 **7**

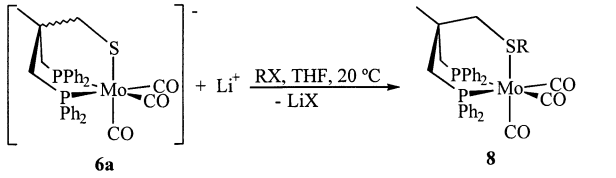
6	M	**7**	M	Cryptand
6a	Li	**7a**	Li	[2,1,1]cryptand
6b	Na	**7b**	Na	[2,2,2]cryptand

In the hope to increase the stability of the salt-like compounds cation scavengers were used to transform the lithium salt **6a** into its lithium [2,1,1]cryptand derivative **7a** and the sodium salt **6b** into its sodium [2,2,2]cryptand analogue **7b**. When the cryptand ligands are added to THF solutions of **6** the salts **7** form and precipitate from the solutions in the form of light-yellow microcrystalline powders. With respect to sensitivity and solubility compounds **7** differ

strongly from compounds **6**. Solutions of **7** in contrast to solutions of **6** do not undergo a rapid color change when exposed to the atmosphere even though a slow color change from light-yellow to light-green is observed on prolonged exposure to air. In constrast to compounds **6** which dissolves in THF, compounds **7** are only very sparingly soluble in this solvent. They are soluble, however, in CH_3CN or CH_3NO_2 without desintegration. The salt of type **7** formed from **6c** by the addition of [2,2,2]cryptand does not dissolve, neither in THF, nor in CH_3CN or CH_3NO_2, so that it could not be characterized. The identity of the anions present in **7** is clear from the negative-ion FAB mass spectra which show the peak for the molecule anion at $m/z = 653$ for both **7a** and **7b**. The close similarity of the anionic parts of **6** and **7** is evident from the close similarity of the relevant NMR data (Tables 1, 2). Shifts as well as coupling constants show only minor differences between the compounds **6** and **7**. Due to the low solubility of compounds **7** and due to an overlap of some of the signals arising from the cryptand ligands a detailed comparison is not possible for all of the signals (Tables 1, 2). The $\tilde{\nu}_{CO}$ IR spectra of compounds **6** and **7** are rather similar as well (Table 3). Taken together the similarity of all the spectral data obtained for **6** and **7** corroborates the structural assignments as elaborated for **6**. Comparing the spectral data obtained for **6a** and **6b** slight differences in chemical shifts as well as in the $\tilde{\nu}_{CO}$ IR data are apparent, the most propable explanation for this observation being that the counter ions are in some form associated with the complexes. It is astonishing to note that the ^{1}H-NMR data of **7a** and **7b** (Tables 1, 2) as well as the IR data (Table 3) of these compounds are slightly different as well. It must be assumed that the compounds are at least in part dissolved as ion pairs such that different properties of the cations are reflected by these data. The identity of the anionic part of **6** and **7** is as well documented by their cyclovoltammogrammes. Both the compounds **6a** and **7a** show a quasi-reversible oxidation at −410 mV vs. S.C.E. The slight difference between the values observed for **7a** and **7b**, if not due to experimental uncertainty, might again indicate that ion pairs are still solvated even with the alkali cation embedded in cryptands. The ratio of the anodic current to the cationic current is around 1.7 and the slope of the anodic current versus the scan rate (50−800 mV) is lower than the one predicted by the square root law[24] for a reversible process. When comparing **7a** and **7b** it is found that the quasi-reversible oxidation occurs at almost the same potential for both compounds (**7b**: −420 mV vs. S.C.E.).

To further corroborate the identity of **6** compound **6a** was treated with alkylating reagents which, based on the constitution assigned to **6**, should lead to the corresponding thioether-functionalized species. In fact **6a** reacts with a variety of electrophilic reagents to produce compounds **8**.

Mass spectra of **8** (FAB or EI) show the molecular ion peak in each case and elemental analyses correspond to the assigned constitution. The NMR data (Tables 1, 2) are as well in accord with their constitution; specifically, they show that the tripod ligand coordinates in a tridentate way.



6a **8**

8	R	X
8a	Me	I
8b	Et	$Et_2O{\cdot}BF_4$
8c	Bzl	Br

This is evidenced by $^3J_{CP}$ coupling constants of around 6 Hz between the coordinated phosphorus atom and the α-carbon atom bonded to the coordinated sulfur center. The coupling constants should be zero if the SR entities would not be coordinated. In the case of **8c** the spectral data obtained for the free ligand[14] show that no P-$C_{\alpha S}$ coupling is observed if not both phosphorus and sulfur atom are coordinated to the same metal center. The presence or absence of diastereotopicity of the protons at the CH_2 groups of the chelate cage (Table 1) does again reflect the symmetry of the compounds as already discussed for **6**. The local symmetry of the $[(CO)_3Mo]$ chromophore reflects the constitutional C_s symmetry which is characteristic for all the compounds **6−8** so that instead of a two-band pattern (A_1, E) as expected for C_{3v} symmetry 3 $\tilde{\nu}_{CO}$ IR bands are observed in general. Only for **8c** the splitting of the E band is not large enough to make the two components derived from it decernible (Table 3).

A comparison of the IR data obtained for **6−8** is rewarding: the anionic compounds **6** and **7** show their absorptions at distinctly lower energy than the neutral compounds **8**. Within each class of compounds the differences are only minor as expected. The dianionic species **6c** has its absorptions at by far the lowest energies. The observed trends are in accord with the well-established rule that the higher the charge density at the metal center the lower the frequencies of the corresponding $\tilde{\nu}_{CO}$ absorptions. With respect to this rule trends observed for compounds **6−8** are in full agreement with their structural assignment derived by other methods as discussed before.

With the identity of **8** established beyond doubt it is clear that the SR group is coordinated in each case. For the type of ligand as present in **6a** and **6b** it had been shown for the neutral complex $[\eta^3\text{-}\{CH_3C(CH_2PPh_2)_2CH_2S\}(CO)_3Mn]$ that alkylation at the sulfur atom may well lead to decoordination with the vacant coordination site being occupied by the nucleofugic group of the alkylation reagent used (e.g. I^- with MeI as the reagent)[16]. This type of reaction is not observed when **6a** is treated with alkylation reagents independent of whether the nucleofugic group is I^- (MeI), Et_2O ($Et_3O{\cdot}BF_4$) or Br^- (BzlBr) even though the neutral manganese compound and the anionic molybdenum compound are isoelectronic ($[(CO)_3Mn]^+$ to $[(CO)_3Mo]$). The coordination of the nucleofugic group of the anionic part of the

electrophile to the metal center can well compete with the coordination of the neutral SR function in the presence of the cationic metal center in $[\eta^3$-$\{CH_3C(CH_2PPh_2)_2CH_2SR\}(CO)_3Mn]^+$ while with the neutral compounds $[\eta^3$-$\{CH_3C(CH_2PPh_2)_2CH_2SR\}(CO)_3Mo]$ (**8**) the anionic nucleophile is not competitive.

Conclusion

Taken together the observations described in this paper allow for the following statements:

– Neopentane-based tripod ligands $CH_3C(CH_2X)(CH_2Y)(CH_2Z)$ (X, Y, Z = PR_2, SR, S^-) are accessible by a convergent set of reactions. The reductive cleavage of SBzl functions in tripod ligands (some of the groups X, Y, Z = SBzl)[15][17][18][19] by lithium under spezialized conditions has a broad scope of application in this context.

– Tripod ligands containing thiolate functions (some of the groups X, Y, Z = S^-) form anionic $[(CO)_3Mo]$ derivatives which contain the ligands in a tridentate binding mode. The coordinatively bound thiolate functions are transformed into coordinated thioether functions upon reaction of the anions with alkylating reagents.

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Experimental Section

General: All manipulations are carried out under argon by means of standard Schlenk techniques. All solvents are dried by standard methods and destilled under argon. Water was degassed by five "pump-thaw" cycles and stored under argon. The $CDCl_3$, CD_2Cl_2 and $[D_8]$THF used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves. The silica gel (Kieselgel z.A. 0.06–0.2 mm, J. T. Baker Chemicals B.V.) used for chromatography was degassed at 1 mbar for 24 h and saturated with argon. – NMR: Bruker Avance DPX 200 at 200.13 MHz (^{1}H), 50.323 MHz (^{13}C{^{1}H}), 81.015 MHz (^{31}P{^{1}H}), 77.779 MHz (^{7}Li); chemical shifts (δ) in ppm with respect to $CDCl_3$ (^{1}H: δ = 7.27; ^{13}C: δ = 77.0), CD_2Cl_2 (^{1}H: δ = 5.32; ^{13}C: δ = 53.5) and $[D_8]$THF (^{1}H: δ = 3.58; ^{13}C: δ = 67.7) as internal standards, and chemical shifts (δ) in ppm with respect to 85% H_3PO_4 (^{31}P: δ = 0) and 1 M LiCl in D_2O (^{7}Li: δ = 0) as external standards. – IR: Bruker FT-IR IFS-66; CaF_2 cells. – MS: Finnigan MAT 8400; FAB: Nibeol (4-nitrobenzyl alcohol) or TEA (triethanol amine) matrices, respectively; EI: 70 eV. Mass spectra are referenced relative to the most abundant Mo isotop ($^{98}_{42}$Mo). Elemental analyses: Microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. With the procedures used carbon contents tend to be found too low in the presence of molybdenum. Some of the analytical data have to be interpreted with this in mind. – Melting points: Gallenkamp MFB-595 010; melting points are not corrected. – Cyclovoltammetry: EG&G Princeton Applied Research model 273; potentials in mV versus S.C.E at a glassy carbon electrode at 25°C; solutions of the compounds: 10^{-3} M in 0.1 M Bu_4NPF_6 in CH_2Cl_2. – **1a–c** and **e** were prepared accordingto ref.[18], **1d** was prepared according to ref.[19]. **4** can be obtained according to ref.[14]. $[(CH_3CN)_3(CO)_3Mo]$ was synthesized as described in ref.[25] and was always freshly prepared (using always fresh batches); [2,1,1]cryptand and [2,2,2]cryptand are abbreviations for 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, respectively. The latter ones and all other chemicals are commercially obtained and used without further purification.

Preparation of **2**: The given amount (vide infra) of **1** was dissolved in THF (50 ml), the solution was cooled to −50°C and liquid NH_3 was added (50 ml). After stirring for 10 min, the given amount (vide infra) of lithium was added. During the reaction the color of the mixture turned from deep blue to red. The reaction was finished when all lithium was consumed (4 h). Then water was added (5 ml) and the NH_3 was cautiously removed by letting the reaction mixture slowly warm up to 20°C. Finally, the THF was removed in vacuo. To the crude product water (50 ml) and diethyl ether (50 ml) were added and the mixture was neutralized with HCl. The phases were separated and the aqueous phase was extracted with diethyl ether (2 × 50 ml). The residue of the combined, dried and concentrated organic phases was purified by chromatography on silica gel in case of **2a**, **2b**, and **2e** (15 cm, Ø = 6 cm). Concentrating the fractions eluted by a mixture of petroleum ether (40/60)/diethyl ether (17:1; TLC control: R_f = 0.4 for **2a** and **2b**/29:1; TLC control: R_f = 0.45 for **2e**) gave the pure products **2a**, **2b** and **2e**. **2c** and **2d** were purified by recrystallization from petroleum ether (40/60) (20 ml). Completion of the crystallization was achieved by cooling the mixture down to −40°C for 1 h.

1a (1.6 g, 3.6 mmol) and Li (50 mg, 7.2 mmol) yielded 1.2 g (95%) of **2a** as a pasty, colorless oil. – $C_{19}H_{25}PS_2$ (348.5): calcd. C 65.48, H 7.23; P 8.89; S 18.40; found C 65.77, H 7.30, P 8.89, S 17.68. – MS (EI); *m/z* (%): 349 (50) [M^+ + 1], 319 (100) [$M^+ - C_2H_5$]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −26.9 (s).

1b (2.3 g, 5.0 mmol) and Li (69 mg, 10.0 mmol) yielded 1.7 g (93%) of **2b** as a pasty, colorless oil (even after prolonged drying, **2b** tenaciously withheld some solvent resulting in somewhat to high carbon values). – $C_{20}H_{27}PS_2$ (362.5): calcd. C 66.26, H 7.51; found C 67.11, H 7.48. – MS (FAB); *m/z* (%): 363 (70) [M^+ + 1], 319 (100) [$M^+ - C_3H_7$]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −26.8 (s).

1c (2.5 g, 5.0 mmol) and Li (138 mg, 10 mmol) yielded 1.4 g (85%) of **2c** as a colorless microcrsystalline solid. – MS (EI); *m/z* (%): 319 (100) [$M^+ - 1$]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −27.3 (s).

1d (2.6 g, 5.0 mmol) and Li (138 mg, 20.0 mmol) yielded 1.6 g (90%) of **2d** as a colorless microcrystalline solid. – $C_{18}H_{23}OPS_2$ (350.5): calcd. C 61.69, H 6.61, P 8.84, S 18.30; found C 61.63, H 6.77, P 8.84 S 18.58. – MS (FAB); *m/z* (%): 349 (100) [M^+]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −26.8 (s).

1e (1.9 g, 4.0 mmol) and Li (112 mg, 16.0 mmol) yielded 980 mg (85%) of **3** as a colorless, microcrystalline solid. – $C_{17}H_{21}PS$ (288.4): calcd. C 70.80, H 7.34; found C 71.26, H 7.64. – MS (FAB); *m/z* (%): 287 (100) [$M^+ - 1$]. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −23.2 (s).

For ^{1}H- and ^{13}C-NMR data see Tables 1 and 2.

Preparation of **5**: Compound **2a** (349 mg, 1 mmol) was dissolved in CH_2Cl_2 (30 ml), solid $[(MeCN)_3(CO)_3Mo]$ was added (302 mg; 1 mmol) and the mixture was stirred for 1 h at room temperature. During the reaction the $[(MeCN)_3(CO)_3Mo]$ slowly dissolved and the color of the solution turned from light-yellow to yellow-brown.

The solvent was removed and the brown residue was chromagraphed on silica gel (15 cm, Ø = 6 cm). Concentrating the fractions eluted by a mixture of petroleum ether (40/60)/CH_2Cl_2 (1:3; TLC control: R_f = 0.75) gave 250 mg (45%) of **5** as a yellow microcrystalline solid, m.p. 150°C (dec.). – $C_{23}H_{35}MoO_4PS_2$ (556.5): calcd. C 49.64, H 4.53, P 5.57, found C 49.88, H 4.85, P 5.55. – MS (EI); *m/z* (%): 558 (8) [M^+], 530 (14) [M^+ – CO], 501 (10) [M^+ – CO – C_2H_5], 473 (6) [M^+ – 2 CO – C_2H_5], 444 (16) [M^+ – 3 CO – C_2H_5 – H]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.0 (s).

For IR -, ^1H- and ^{13}C-NMR data see Tables 1–3.

Preparation of **6**: 1 mmol of **2d** or **4** (vide infra) was dissolved in 30 ml of THF, the solution was cooled to 0°C and treated with NaH or *n*-butyllithium (vide infra). After stirring for 30 min, solid [$(MeCN)_3(CO)_3Mo$] (302 mg, 1 mmol) was added. During the reaction the color of the mixture turned light-brown. After stirring for another 30 min, the reaction mixture was concentrated to 3–5 ml and 30 ml of petroleum ether (40/60) was added. If oily products were obtained the mixtures were treated twice with 30 ml of petroleum ether (40/60) in an ultrasonic bath. The pure yellow microcrystalline products were obtained in quantitative yields by removing the solvent in vacuo. In all cases the products contained two molecules of THF per formula unit. When compounds **6** were prepared for a consecutive reaction the purification step did not need to be applied e.g. preparation of **7** or **8**.

4 (472 mg, 1 mmol) and *n*-butyllithium (2.5 M, 0.4 ml, 1 mmol) yielded 800 mg of **6a** · 2 THF. – $C_{32}H_{29}LiMoO_3P_2S \cdot 2\ C_4H_8O$ (800.5): calcd. C 59.85, H 5.65, P 7.72; found C 58.51, H 6.13, P 7.30. – $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = 21.6 (s). – ^7Li NMR ([D_8]THF): δ = –0.33.

4 (472 mg, 1 mmol) and NaH (24 mg, 1 mmol) yielded 820 mg of **6b** · 2 THF. – $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = 19.8 (s).

2d (350 mg, 1 mmol) and NaH (48 mg, 2 mmol) yielded 720 mg of **6c** · 2 THF. – $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = 14.9 (s).

For IR, ^1H- and ^{13}C-NMR data see Tables 1–3.

Preparation of **7**: To a solution of 1 mmol of **6a** · 2 THF or **6b** · 2 THF (vide infra) in THF (30 ml) the given cryptand (vide infra) was added. While stirring the mixtures for 30 min, yellow precipitates formed. The precipitates were separated from the solvent and washed with petroleum ether (40/60). Drying in vacuo gave the pure yellow microcrystalline products in quantitative yields.

6a · 2 THF (800 mg, 1 mmol) and [2,1,1]cryptand (288 mg, 1 mmol) yielded 946 mg of **7a**. – $C_{46}H_{57}LiMoN_2O_7P_2S$ (946.9): calcd. C 58.35, H 6.07, N 2.96, P 6.54; found C 58.04, H 6.43, N 2.76, P 6.32. – MS (FAB negative); *m/z* (%): 653 (100) [M^-]. – $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ = –20.4 (s). – ^7Li NMR ([D_8]THF): δ = –1.37.

6b · 2 THF (820 mg, 1 mmol) and [2,2,2]cryptand (376 mg, 1 mmol) yielded 1050 mg of **7b**. – $C_{50}H_{65}MoN_2NaO_9PS_2$ (1049.9): calcd. C 57.19, H 6.24, N 2.67; found C 58.51, H 6.31, N 2.48. – MS (FAB negative); *m/z* (%): 653 (60) [M^-]. – $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = –19.8 (s).

For IR, ^1H- and ^{13}C-NMR data see Tables 1–3.

Preparation of **8**: To a solution of **6a** · 2 THF (800 mg, 1 mmol) in THF (30 ml) the given alkylation reagent (vide infra) was added and the mixture was stirred for 2 h. The solvent was removed and the brown residue was chromagraphed on silica gel (15 cm, Ø = 6 cm). Concentrating the fractions eluted by a mixture of petroleum ether (40/60)/CH_2Cl_2 (1:3; TLC control: R_f = 0.71–0.75) gave the pure compounds **8** as yellow microcrystalline solids. While **8a** and **8b** were obtained solvent-free, **8c** crystallized with 0.5 equivalents of CH_2Cl_2 per formula unit. The obtained yields were: **8a**: 488 mg (73%), m.p. 195°C (dec.); **8b**: 409 mg (60%), m.p. 188°C (dec.); **7c**: 493 mg (70%), m.p. 205°C (dec.).

8a: MeI (426 mg, 3 mmol). – $C_{33}H_{32}MoO_3P_2S$ (666.6): calcd. C 59.28, H 4.83, P 9.27; found C 58.31, H 4.87, P 9.09. – MS (EI); *m/z* (%): 668 (28) [M^+], 640 (40) [M^+ – CO], 612 (30) [M^+ – 2 CO], 584 (100) [M^+ – 3 CO]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = –18.1 (s).

8b: $Et_3O{\cdot}BF_4$ (513 mg, 3 mmol). – $C_{34}H_{34}MoO_3P_2S$ (680.6): calcd. C 59.82, H 5.02, P 9.08; found C 59.12, H 5.30, P 8.97. – MS (EI); *m/z* (%):682 (32) [M^+], 654 (46) [M^+ – CO], 626 (20) [M^+ – 2 CO], 596 (100) [M^+ – 3 CO]. – $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = –22.5 (s).

8c: BzlBr (380 mg, 3 mmol). – $C_{39}H_{36}MoO_3P_2S \cdot 0.5\ CH_2Cl_2$ (785.2): calcd. C 60.42, H 4.75; found C 60.01, H 4.62. – MS (FAB); *m/z* (%): 744 (28) [M^+], 660 (46) [M^+ – 3 CO], 569 (14) [M^+ – 3 CO – Bzl], 471 (5) [M^+ – 3 CO – Bzl – Mo]. – $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = –18.0 (s).

For IR, ^1H- and ^{13}C-NMR data see Tables 1–3.

☆ Dedicated to Prof. *H. P. Latscha* on the occasion of his 60th birthday.

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