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## Complexes wits a Thioalkyl-Bridged M-P-Bond from Metallo(Alkylthio)Phosphanes

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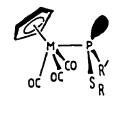
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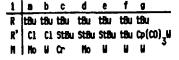
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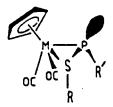
COMPLEXES WITH A THIOALKYL-BRIDGED M-P-BOND FROM METALLO (ALKYLTHIO) PHOSPHANES

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Metallation of alkylthio(chloro)phosphanes ClP(R')S-R (R = i-Pr, tBu; R' = tBu, St-Bu) and  $Cl_2P-S-tBu$  with  $Na[M(CO)_3Cp]$  (M = Cr, Mo, W) yields the metallo-(alkylthio)chloro-, metallo-bis(alkylthio)-, metallo-(alkylthio)(alkyl)phosphanes (1a-f) or the bis(metallo)(alkylthio)phosphane (1g) respectively.







		b			e_	<u>f</u>	9	<u>h</u>
R	tBu	tBu	tBu	tBu	ifr	tibu	tBu	tBu
R*	tBu	StBu	StBu	Cp(CO)_W	tBu	tBu	tBu Cp(CO) <sub>3</sub> No	φ(α) <sub>*</sub> N
Ħ	W	No	u	W 3	No	No	Mo	Ho 3

Due to the bulkiness of the P-bonded non metal ligands the metallo-(alkylthio)phosphanes 1d-g can be easily decarbonylated either thermally or via reaction with Ni(CO)<sub>4</sub> to give the metallacycles 2a-d. 2e,f / 2g,h are obtained directly from Na[Mo(CO)<sub>3</sub>Cp] and the chlorophosphines / 1a,b. 2a-h represent a valence tautomer of the originally expected metal to phosphorus double bonded species Cp(CO)<sub>2</sub>M=P(R')SR. The proposed structure of 2h is proved by reaction with Li-S-iPr yielding 2b. The combination of a thioalkyl ligand with a bulky amino- or phenoxy group preferentially yields the M=P-isomer. This fact is demonstrated by the generation of Cp(CO)<sub>2</sub>W=P(R)S-iPr from Cp(CO)<sub>2</sub>W=P(R)Cl (R = 2.2.6.6 tetramethylpiperidyl, 2.6. di(tert.butyl)phenoxy) and Li-S-iPr.