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Transition Metal Substituted Phosphanes, Arsanes and Stibanes. XLIII [1]
Thermal Treatment of $Cp(OC)_3W$-Substituted Arsanes and Arsinesulfides: Inter- and Intramolecular Ligand Exchange with CO-Substitution

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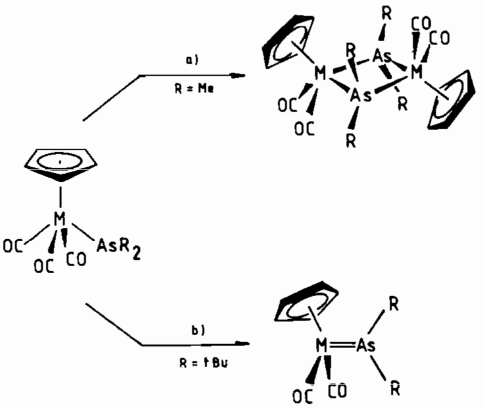
Metallo–arsanes $Cp(OC)_3M–AsR_3$ (M = Mo, W; R = Me, t-Bu) possess a strong tendency towards coordination to metal centers, which indicate high Lewis basicity of the arsenic atom [2, 3]. Aggregation to four-membered ring systems by *inter*molecular CO-substitution on thermal or photochemical treatment, which is preferred by the methyl derivatives (eqn. 1a), has to be regarded as a special case of coordination reaction [2, 4]. However the metallo–arsanes in which the arsenic-donor center bears th bulky t-butyl group undergo an *intra*molecular CO-substitution reaction leading to the formation of mononuclear species with a metal–arsenic double bond (eqn. 1b) [5].

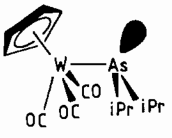


(1)

A similar situation is valid for metallo-arsinesulfides $Cp(OC)_3M–AsR_2(S)$, which are formed readily through oxidative addition of elemental sulfur to the metallo–arsanes [6]. A new nucleophilic center in a β-position to the metal atom is established, which can induce in principle formation of either three- or six-membered ring systems $[Cp(CO)_2M–AsR_2(S)]_x$ (x = 1, 2). For R = t-Bu an inorganic cyclopropane derivative has been obtained and structurally characterized [7].

We were interested in determining whether decarbonylation of metallo-arsanes or metallo-arsine sulfides, with either the less bulky isopropyl group or a combination of the tert-butyl and a methyl group as substituents would give the M=As double bond or the three membered ring species $Cp(OC)_2W–AsR_2–S$ respectively.

The metallo-di(isopropyl)arsane *1* can be synthesized in 80% yield by nucleophilic metallation of $(i\text{-}Pr)_2AsCl$ with $Na[W(CO)_3Cp]$ in benzene or toluene. The chiral arsane *3* is prepared in a two-step reaction starting with $t\text{-}Bu\text{-}AsCl_2$ and $Na[W(CO)_3Cp]$ to give $Cp(OC)_3W–As(t\text{-}Bu)Cl$ (*2*), which is then methylated with methyl lithium [8].



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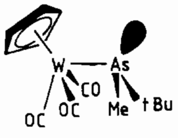
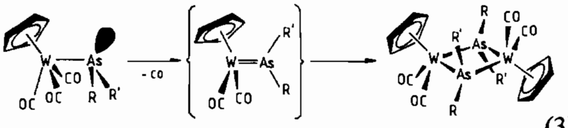


3

(2)

1, 3 undergo *inter*molecular CO-substitution on heating in toluene at 100 °C, leading to the formation of the four membered heterocycles *4a, b*.



(3)

	4a	b
R	iPr	Me
R'	iPr	tBu

The decarbonylation reaction (2) demonstrates that even a small reduction in size of the alkyl substituents concurrently reduces kinetic stabilization of the doubly bonded W = As-species *A* to such an extent that immediate aggregation occurs.

The ^1H-spectrum of *4b* exhibits only one resonance for each of the cyclopentadienyl, *tert* butyl and methyl groups, indicating that only one stereoisomer exists in solution [8]. Since all known homologs of *4a, b* [2, 4, 9, 10] adopt a structure with the two cyclopentadienyl rings *trans* to each other, and since two *tert* butyl groups on the same side of the ring would cause high steric crowding, we conclude that the centrosymmetric isomer depicted in eqn. (3) is formed. The arsanes, *1, 3* react readily with elemental sulfur in methylcyclohexan at 0 °C to give the corresponding arsine sulfides *5a, b* as orange-red air stable crystals.

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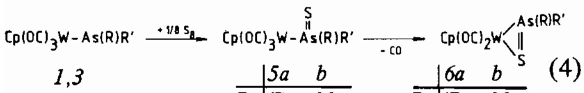
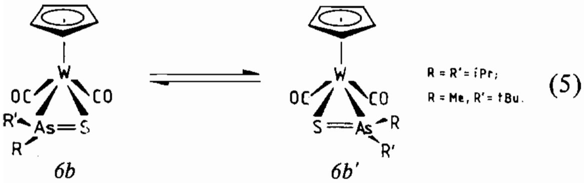


1,3

	5a	*b*		*6a*	*b*
R	iPr	Me	R	iPr	Me
R'	iPr	tBu	R'	iPr	tBu

5a, b are converted on refluxing in pentane (CO-elimination !) to the complexes *6a, b,* with the thioarsinyl ligand in a side-on coordinated fashion, the latter complexes being obtained as deep red-brown crystals after low temperature crystallization. In contrast to the result of eqn. (3) for the arsanes *1, 3,* even with smaller alkyl groups there is still preference for *intra*-molecular CO-substitution in the case of the arsine-sulfides *5a, b.* Below -10 °C the diastereotopic methyl groups of the *iso*propyl unit show the expected eight line pattern in the ^{1}H-NMR spectrum, which collapse at -6 °C to four lines, indicating rapid rotation of the $R_2As(S)$-ligand. The $\Delta G^{\ddagger}_{267}$ value for this process is calculated to be 14.0 kcal/mol [7].



6b *6b'*

Interestingly *6b* shows at room temperature only one set of ^{1}H-NMR resonances, which broaden between +15 and -10 °C and which become sharp again at low temperature. This finding suggests the presence of the two diastereomers *6b, 6b'* at higher temperatures, with *6b* (having the *tert*-butyl group pointed away from the cyclopentadienyl-unit) predominating at lower temperature. Interconversion of *6b* and *6b'* is achieved by simple rotation of the η^2-bound thioarsinyl group.

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References

1 Part XLII; M. Kuksza, U. Wanka and W. Malisch, *J. Organomet. Chem.,* in press.

2 W. Malisch, M. Kuhn, W. Albert and H. Rössner, *Chem. Ber., 112,* 3318 (1980).

3 R. Müller and H. Vahrenkamp, *Chem. Ber., 110,* 3910 (1977).

4 P. Panster and W. Malisch, *Chem. Ber., 109,* 3842 (1976).

5 M. Luksza, S. Himmel and W. Malisch, *Angew. Chem., 95,* 418 (1983); *Angew. Chem., Int. Ed. Engl., 22,* 416 (1983).

6 W. Malisch, R. Janta and G. Künzel, *Z. Naturforsch., 34b,* 599 (1979).

7 W. Malisch, M. Luksza and W. S. Sheldrick, *Z. Naturforsch., 36b,* 1580 (1981)

8 *1*: yellow-orange crystals; m.p. 36 °C; ^{1}H-NMR (C_6H_6): δ = 4.75 (s, 5H, H_5C_5), 2.43 (dsept, $^3J_{HCCH}$ = 6.8 Hz, 2H, HCAs), 1.42 (d, $^3J_{HCCH}$ = 11.0 Hz, 6H, H_3CCAs), 1.27 (d, $^3J_{HCCH}$ = 11.0 Hz, 6H, H_3CCAs).
IR (C_6H_6): νCO_s = 1990(s); νCO_{as} = 1911 (vs), 1896 (vs).
2: yellow crystals; m.p. 99.5 °C; ^{1}H-NMR (C_6H_6): δ = 4.80 (s, 5H, H_5C_5), 1.59 (s, 9H, H_3CCAs). IR (pentane): νCO_s = 2010(s); νCO_{as} = 1951(s), 1923(vs).
3: Orange powder; m.p. 57–60 °C; ^{1}H-NMR (C_6H_6): δ = 4.70(s, 5H, H_5C_5), 1.50 (s, 3H, H_3CAs), 1.39 (s, 9H, H_3CCAs). IR (pentane): νCO_s = 1999(s); νCO_{as} = 1929 (vs), 1913 (vs).
4a: deep red powder; m.p. 164 °C; ^{1}H-NMR (C_6H_6): δ = 5.13 (s, 10H, H_5C_5), 2.17 (m, $^3J_{HCCH}$ = 6.6 Hz, 4H, *H*CAs), 1.33 (d, $^3J_{HCCH}$ = 6.6 Hz, 12H, H_3CCAs), 1.27 (d, $^3J_{HCCH}$ = 6.6 Hz, 12 H, H_3CCAs). IR (benzene): νCO_s = 1919(vs); νCO_{as} = 1846(s).
4b: brown red powder; m.p. 136 °C; ^{1}H-NMR (C_6H_6): δ = 4.97 (s, 10H, H_5C_5), 2.09 (s, 6H, H_3CAs, 1.58 (s, 18H, H_3CCAs). IR (pentane): νCO_s = 1941(vs); νCO_{as} = 1866(s).
5a: orange red crystals; m.p. 49 °C; ^{1}H-NMR (C_6H_6): δ = 4.79 (s, 5H, H_5C_5), 2.22 (dsept, $^3J_{HCCH}$ = 6.8 Hz, 2H, HCAs), 1.38 (d, $^3J_{HCCH}$ = 11.0 Hz, 6H, H_3CCAs), 1.27 (d, 6H, H_3CCAs). IR (benzene): νCO_s = 2020(s); νCO_{as} = 1936(vs), 1918(s).
5b: orange red crystals; m.p. 74–75 °C; ^{1}H-NMR (C_6H_6): δ = 4.89(s, 5H, H_5C_5), 1.33 (s, 3H, H_3CAs), 1.35 (s, 9H, H_3CCAs). IR (methylcyclohexane): νCO_s = 2026(s); νCO_{as} = 1944(vs).
6a: deep red crystals; m.p. 77 °C; ^{1}H-NMR (C_6H_6): δ = 5.12 (s, 5H, H_5C_5), 2.35 (m, 2H, $HCCH_3As$), 1.11 (d, $^3J_{HCCH}$ = 7.0 Hz, 6H, H_3CCAs), 1.08 (d, $^3J_{HCCH}$ = 7.0 Hz, 6H, H_3CCAs). IR (benzene): νCO_s = 1940(vs); νCO_{as} = 1852(s).
6b: red violet crystals; m.p. 110 °C (dec.); ^{1}H-NMR (C_6H_6): δ = 5.15 (s, 5H, H_5C_5), 1.53 (s, 3H, H_3CAs), 1.28 (s, 9H, H_3CCAs). IR (benzene): νCO_s = 1941 (vs); νCO_{as} = 1852(s).

9 R. G. Hayter, *J. Am. Chem. Soc., 86,* 823 (1964).

10 E. Gross and W. Malisch, unpublished results.