

only small amounts of $\text{Na}_4\text{Cr}(\text{CO})_4$ by its low conversion (2–3% yield) to **2a** (see Table I). The reduction of coordinated or uncoordinated norbornadiene by sodium in liquid ammonia may be responsible for this unfavorable results.^{13a} Also, $\text{Na}_2\text{M}(\text{CO})_5$ ^{13b} (M = Cr or W) is not converted to $\text{Na}_4\text{M}(\text{CO})_4$ either because it is stable to reduction (for M = Cr or W in HMPA or for M = Cr in NH_3) or decomposes (for M = W in NH_3) to an uncharacterized brown powder which contains no $\text{Na}_4\text{W}(\text{CO})_4$ but rapidly converts Ph_3SnCl to hexaphenylditin. Reduction of $(\text{TMEDA})\text{M}(\text{CO})_4$ by sodium metal in HMPA at room temperature provides $\text{Na}_2\text{M}(\text{CO})_5$ as the only carbonyl containing products. Reductions using other electropositive metals will be described in a subsequent paper.

- (13) (a) B. R. Ortiz de Montellano, B. A. Loving, T. C. Shields, and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 3365 (1967); (b) J. E. Ellis and G. P. Hagen, *Inorg. Chem.*, **16**, 1357 (1977).
- (14) Reductive coupling of coordinated carbon monoxide¹⁵ to yield a π -acetylenediolate dianion complex (see below) could also explain the abnormally low $\nu(\text{CO})$ values observed in these species. An analogous π -bisaminoacetylene complex has recently been prepared from the reductive coupling of coordinated isocyanides (C. T. Lam, P. Corfield, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 617 (1977)). We have no chemical evidence for reductive coupling in our compounds; i.e., all of the reactions of the "tetraanions" give rise to derivatives containing terminal carbonyls. However, as depicted, it is possible that reductive coupling of CO can be reversed on addition of an electrophile to yield the observed derivatives.
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- (15) Free carbon monoxide reacts with sodium in liquid ammonia to form disodium acetylenediolate and other products (V. M. Sinclair, R. A. Davies and J. L. Drummond, *Chem. Soc. Spec. Publ.*, **No. 22**, 260 (1967)).
- (16) Yields are moderate to low (~30% **2a**; ~1% **2b**; ~50% **2c**). Hexa-phenylditin also forms in these reactions. Substantially better yields (~60–70%) of **2** are obtained from the reaction of $(\text{TMEDA})\text{M}(\text{CO})_4$ (M = Cr, Mo, and W) with 2 equiv of Ph_3SnLi in THF followed by metathesis with Et_4NBr in ethanol.
- (17) Anal. Calcd for $\text{C}_{56}\text{H}_{70}\text{CrN}_2\text{O}_4\text{Sn}_2$ (**2a**): C, 59.81; H, 6.27; N, 2.49; Sn, 21.11. Found: C, 59.78; H, 6.17; N, 2.43; Sn, 21.17. Anal. Calcd for $\text{C}_{56}\text{H}_{70}\text{MoN}_2\text{O}_4\text{Sn}_2$ (**2b**): C, 57.56; H, 6.04; N, 2.40. Found: C, 57.47; H, 6.13; N, 2.28. Anal. Calcd for $\text{C}_{56}\text{H}_{70}\text{W}_2\text{O}_4\text{Sn}_2$ (**2c**): C, 53.54; H, 5.62; N, 2.23. Found: C, 53.20; H, 5.58; N, 2.68. The total yield of derivatives (**2c** and **3c**) from $\text{Na}_4\text{W}(\text{CO})_4$ is ~70%.
- (18) Yields of analytically pure samples in these reactions are only moderate (~35% for **3a–c**) owing in part to incomplete conversion of **2** to **3**. However, **3** is easily separated from **2** by virtue of its moderate solubility in THF, in which **2** is insoluble. Anal. Calcd for $\text{C}_{66}\text{H}_{65}\text{CrNO}_4\text{Sn}_3$ (**3a**): C, 58.97; H, 4.87; N, 1.04; Sn, 26.49. Found: C, 59.25; H, 5.05; N, 0.85; Sn, 26.32. Anal. Calcd for $\text{C}_{66}\text{H}_{65}\text{MoNO}_4\text{Sn}_3$ (**3b**): C, 57.10; H, 4.72; N, 1.01; Sn, 25.65. Found: C, 56.89; H, 4.36; N, 1.77; Sn, 25.34. Anal. Calcd for $\text{C}_{66}\text{H}_{65}\text{WNO}_4\text{Sn}_3$ (**3c**): C, 53.70; H, 4.44; N, 0.95; Sn, 24.12. Found: C, 53.37; H, 4.18; N, 1.25; Sn, 24.39.
- (19) Numerous examples of seven-coordinate molybdenum and tungsten carbonyl complexes exist (e.g., $\text{M}(\text{CO})_4\text{L}_3^-$) for which there are no chromium analogues (see M. W. Anker, R. Colton, and I. B. Tomkins, *Rev. Pure Appl. Chem.*, **18**, 23 (1968)). However, seven-coordinate chromium carbonyl complexes with polydentate ligands are known (e.g., $[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{Br}]\text{Br}$, J. Lewis, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 3009 (1964)).
- (20) Triphenylstannyllithium reacts with $[\text{Et}_4\text{N}][(\text{Ph}_3\text{Sn})_3\text{Cr}(\text{CO})_4]$ (**3a**) to provide essentially quantitative yields of $(\text{Ph}_3\text{Sn})_2\text{Cr}(\text{CO})_4^{2-}$ and hexaphenylditin. Infrared studies show that HMPA causes complete heterolytic cleavage of one Sn–Cr bond in **3a** to yield $(\text{Ph}_3\text{Sn})_2\text{Cr}(\text{CO})_4^{2-}$. Analogous heterolytic cleavages of tin–metal bonds by polar solvents have been known for several years (e.g., see A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **36**, 113 (1972)); however, generally the degree of solvation of the tin cation is unknown.
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MNDO Parameters for Third Period Elements

Sir:

The MINDO/3 method¹ suffers from well-known problems¹ and, in the case of compounds containing heteroatoms and its use for third period elements (Si, P, S, Cl), is further restricted by the availability of parameters for them only for limited combinations of them with other elements^{2,3} and without inclusion of 3d AOs. Furthermore, recent work⁴ has

Table I. MNDO Parameters for Third Row Elements

Optimized	Si	P	S	Cl
U_{ss} , eV	-40.568292	-56.143360	-75.239152	-100.227166
U_{pp} , eV	-28.089187	-42.851080	-57.832013	-77.378667
ζ_s , au	1.435306	2.108720	2.613591	3.784645
ζ_p , au	1.435306	1.785810	2.034393	2.036263
β_s, β_p , eV	-4.256218	-6.791600	-11.142231	-14.262320
α , \AA^{-1}	2.1961078	2.4152800	2.4916445	2.542201

Table II. MNDO Parameters for Third Row Elements

Derived	Si	P	S	Cl
H_f^A , kcal mol ⁻¹	108.39	75.57	66.40	28.99
E_{el}^A , eV	-90.53496	-152.95996	-235.45636	-353.137667
D_1 , \AA	0.744999	0.536030	0.435589	0.263889
D_2 , \AA	0.616918	0.495834	0.435248	0.434848
ρ_0 , \AA	0.733128	0.622778	0.558953	0.478996
ρ_1 , \AA	0.768732	0.541911	0.449254	0.328218
ρ_2 , \AA	0.664346	0.531356	0.468321	0.435983

uncovered a discrepancy between the published² results for compounds of phosphorus and those calculated using the published¹ parameters which are also included in our MINDO/3 computer program, and similar, though smaller discrepancies have now been found for silicon and sulfur.⁵ Apparently an earlier set of parameters was inadvertently inserted in our final computer program and hence in the published list.¹ The results for chlorine³ are, however, correct.⁵

In the meantime we have parameterized the MNDO method⁶ for these elements (Si, P, S, Cl) and the results are, as expected, better than the published² MINDO/3 ones. MNDO has the further advantage of using only atomic parameters; so calculations can be carried out for any combinations of these elements with those already parameterized (H,⁷ Be,⁸ B,⁹ C,⁷ N,⁷ O,⁷ F¹⁰). As yet, 3d AOs have not been included in MNDO; so the parameters refer only to compounds of these elements in their characteristic valence states (Si^{IV}, P^{III}, S^{II}, Cl^I). The calculated heats of formation for compounds of, e.g., P^V and S^{VI} are too positive by very large amounts.

This work will be repeated in full in due course but unexpected circumstances have delayed its publication. In view of the unexpected problems with MINDO/3 and the very wide demand for some procedure applicable in particular to compounds of P, we are therefore reporting the parameters for Si, P, S, and Cl here (Tables I and II). Computer programs for MNDO are available from Q.C.P.E., both ours and one written in a more general version of FORTRAN by Dr. W. Thiel.

References and Notes

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