The most important effect of alkylation is the decreased Ti—Cl distance. This can be rationalized in terms of the inductive electron donation by the alkyl groups and is in accord with the suggestions of enhanced electron-releasing ability of a peralkylated C_5R_5 group based on chemical reactivity. This can be seen as increasing electron density in orbitals which are of bonding character for the Ti—Cl bonds. The strengthening of these bonds corresponds to the enhanced chemical stability for $(C_5R_5)TiX_3$ compounds. For $(C_5H_5)_2TiCl_2$, the effects are much smaller and the steric interference between the alkylated rings is probably more important (McKenzie *et al.*, 1975).

The crystal contains no significantly short intermolecular distances, and the packing is dominated by CH_3–CH_3 and CH_3–Cl contacts.

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Octacarbonyl-bis(μ-{iodo[tetracarbonyl(triphenylphosphine)rhenio]stannio(IV)})-dirhenium, $[Re_2(CO)_8\{Sn(I)Re(CO)_4[P(C_6H_5)_3]\}_2]$

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Abstract. $M_r = 2208{\cdot}7$, monoclinic, $P2_1/c$, $a = 9{\cdot}096\ (7)$, $b = 29{\cdot}271\ (9)$, $c = 11{\cdot}291\ (7)$ Å, $\beta = 93{\cdot}73\ (5)°$, $U = 3000$ Å^3, $Z = 2$, $D_x = 2{\cdot}445$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}5$ mm^{-1}, $F(000) = 2012$, $T = 294\ (1)$ K. Final $R = 0{\cdot}034$ for 2978 observed reflections. The central fragment of the molecule consists of a planar Re_2Sn_2 rhombus with an Re—Re bond [r(Re—Re) = 3·176 (1) Å] across the metal ring. The iodine and $Re(C_{18}H_{15}P)(CO)_4$ ligand pairs bonded to Sn are in the *trans* position with respect to the ring plane.

Introduction. In the course of our investigation on the influence of different metal atoms on the geometry of four-membered metal rings in clusters of the type $[Mn_2(CO)_8\{\mu\text{-}M(X)Mn(CO)_5\}_2]$ (M = Ge, X = Br, I; M = Sn, X = Br, Cl) (Preut & Haupt, 1980) we have prepared the compound $[Re_2(CO)_8\{\mu\text{-}Sn(I)\text{-}Re(C_{18}H_{15}P)(CO)_4\}_2]$ and determined the crystal structure. The result of the structure analysis is furthermore used for our study of a relationship between packing forces and the geometry of the molecules in such crystals.

Experimental. The yellow crystals were prepared by a reaction of SnI_2 with $[Re_2(C_{18}H_{15}P)_2(CO)_8]$ in xylene at 443 K during a reaction time of four weeks in a bomb tube.

$\omega/2\theta$ scan, scan speed of 0·74–3·33° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, crystal size 0·3 × 0·3 × 0·4 mm, lattice parameters from least-squares fit with 24 reflections in the range $10{\cdot}6 \leq \theta \leq 13{\cdot}9°$; three standard reflections, recorded every 4 h: only random deviations; 4589 reflections measured, $2 \leq \theta \leq 23°$, h 0→9, k 0→32, l −12→12; after averaging: 2978 observed reflections with $F_o > 3\sigma(F_o)$, Lorentz–polarization correction, absorption correction *via* ψ-scans; systematic absences: $(h0l)$ $l = 2n+1$ and $(0k0)$ $k = 2n+1$, space group $P2_1/c$; structure solution with

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*MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980)–positions of Re, Sn, I and P revealed, ΔF syntheses and full-matrix least-squares refinements with anisotropic temperature factors for all non-H atoms; before last three refinement cycles the H atoms were placed in geometrically calculated positions and a common temperature factor for H atoms refined to $B = 6\ (1)$ Å^2; at the end of the refinement the C—H distances are in the range 0·97 (2) to 0·99 (2) Å and the C—C—H angles are in the range 118 (2) to 121 (2)°; complex neutral-atom scattering factors from Cromer (1974) and Cromer & Waber (1974); least-squares refinement based on F^2 and 353 refined parameters, $R = 0{\cdot}034$, unit weights, $(\Delta/\sigma)_{\max} = 0{\cdot}02$, no significant features in a final ΔF synthesis; programs: Enraf–Nonius *SDP* (Frenz, 1981), *ORTEP*II (Johnson, 1976), *POP*1 (van de Waal, 1976).

Discussion. The structure of the title compound is shown in Fig. 1 (*ORTEP*) and in a stereoscopic view in Fig. 2 (*POP*1). Atomic parameters are given in Table 1,* bond lengths and angles in Table 2.

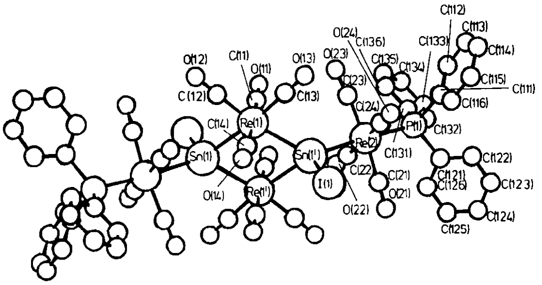

Fig. 1. General view of the molecule.

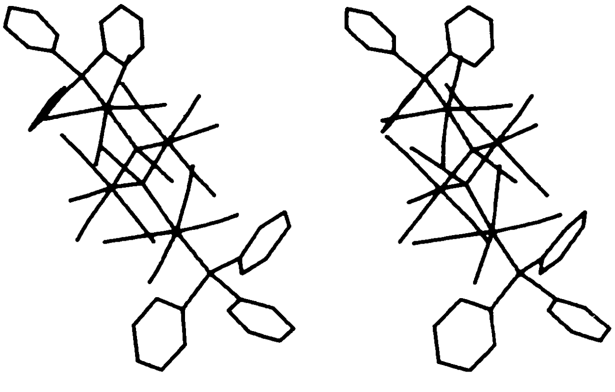

Fig. 2. Stereoscopic view of the molecule.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Re(1)	0·86435 (7)	0·01168 (2)	0·90936 (5)	2·77 (1)
Re(2)	0·83381 (7)	0·11382 (2)	0·25682 (5)	2·68 (1)
I(1)	0·8428 (1)	−0·13520 (4)	1·0100 (1)	4·91 (3)
Sn(1)	1·0233 (1)	−0·06934 (4)	0·91260 (9)	2·84 (2)
P(1)	1·3050 (4)	−0·1541 (1)	0·5989 (3)	2·86 (8)
O(11)	1·064 (2)	0·0580 (6)	0·729 (1)	7·7 (4)
O(12)	0·654 (1)	0·0937 (5)	0·873 (1)	6·4 (4)
O(13)	0·720 (2)	−0·0424 (5)	0·701 (1)	7·1 (4)
O(14)	1·350 (1)	0·0292 (5)	0·914 (1)	6·5 (3)
O(21)	1·235 (1)	−0·1838 (5)	0·946 (1)	6·4 (3)
O(22)	1·446 (2)	−0·0592 (6)	0·827 (2)	9·4 (4)
O(23)	1·049 (2)	−0·0384 (6)	0·568 (1)	10·7 (5)
O(24)	0·870 (1)	−0·1646 (6)	0·682 (1)	7·6 (4)
C(11)	0·996 (2)	0·0404 (7)	0·800 (1)	4·2 (4)
C(12)	0·736 (2)	0·0639 (6)	0·888 (1)	4·0 (4)
C(13)	0·771 (2)	−0·0226 (6)	0·779 (2)	4·2 (4)
C(14)	0·729 (2)	−0·0162 (6)	1·023 (1)	4·1 (4)
C(21)	1·212 (2)	−0·1576 (6)	0·869 (1)	4·1 (4)
C(22)	1·347 (2)	−0·0799 (6)	0·796 (2)	5·3 (4)
C(23)	1·097 (2)	−0·0669 (7)	0·631 (2)	6·6 (5)
C(24)	0·981 (2)	−0·1455 (7)	0·704 (2)	5·3 (5)
C(111)	1·191 (2)	−0·1806 (6)	0·476 (1)	3·2 (3)
C(112)	1·203 (2)	−0·1681 (8)	0·360 (2)	5·7 (5)
C(113)	1·109 (3)	−0·1874 (9)	0·274 (2)	7·2 (6)
C(114)	1·006 (2)	−0·2185 (8)	0·300 (2)	6·6 (5)
C(115)	0·994 (2)	−0·2301 (7)	0·416 (2)	5·2 (5)
C(116)	1·086 (2)	−0·2108 (6)	0·505 (2)	4·3 (4)
C(121)	1·415 (1)	−0·2016 (5)	0·658 (1)	3·0 (3)
C(122)	1·419 (2)	−0·2431 (6)	0·603 (2)	4·8 (4)
C(123)	1·504 (2)	−0·2780 (7)	0·652 (2)	6·6 (6)
C(124)	1·589 (2)	−0·2721 (7)	0·753 (2)	5·5 (5)
C(125)	1·592 (2)	−0·2313 (8)	0·807 (2)	5·7 (5)
C(126)	1·507 (2)	−0·1944 (6)	0·761 (2)	4·2 (4)
C(131)	1·435 (2)	−0·1196 (7)	0·523 (1)	4·4 (4)
C(132)	1·572 (2)	−0·1376 (7)	0·500 (2)	5·4 (5)
C(133)	1·668 (2)	−0·1115 (9)	0·433 (2)	7·4 (6)
C(134)	1·622 (2)	−0·0679 (8)	0·391 (2)	6·9 (6)
C(135)	1·493 (2)	−0·0522 (8)	0·415 (2)	7·1 (6)
C(136)	1·399 (2)	−0·0760 (7)	0·480 (2)	5·2 (5)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Symmetry code: (i) $2 - x, \bar{y}, 2 - z$.

Re(1)–Sn(1)	2·776 (1)	Sn(1)–I(1)	2·802 (2)
Re(1)–Sn(1$^{\rm i}$)	2·769 (1)	Re(2)–Sn(1$^{\rm i}$)	2·714 (1)
Re(1)–Re(1$^{\rm i}$)	3·176 (1)	Re(2)–P(1)	2·430 (4)
Re(1)–Sn(1$^{\rm i}$)–Re(1$^{\rm i}$)	69·89 (3)	Re(1$^{\rm i}$)–Sn(1$^{\rm i}$)–I(1)	109·42 (4)
Re(1)–Sn(1$^{\rm i}$)–I(1)	105·97 (4)	Re(2)–Sn(1$^{\rm i}$)–I(1)	105·43 (4)
Re(1)–Sn(1$^{\rm i}$)–Re(2)	129·26 (4)	Sn(1)–Re(1)–Sn(1$^{\rm i}$)	110·11 (3)
Re(1$^{\rm i}$)–Sn(1$^{\rm i}$)–Re(2)	132·32 (4)	Sn(1)–Re(2)–P(1)	177·03 (9)

The unit cell contains two centrosymmetrical molecules. As in the compounds $[\mathrm{Mn_2(CO)_8}\{\mu\text{-}\mathrm{Sn}(X)\mathrm{Mn(CO)_5}\}_2]$ (X = Cl, Br) (Haupt, Preut & Wolfes, 1978; Preut & Haupt, 1976) the acute angles at the Sn atoms in the planar four-membered ring indicate a bond across the ring between the transition-metal atoms. This bond is demanded by the 18-electron rule for these transition-metal atoms. The present study shows that the Re—Re interaction across the ring is stronger than the corresponding Mn—Mn interaction in $[\mathrm{Mn_2(CO)_8}\{\mu\text{-}\mathrm{Sn}(X)\mathrm{Mn(CO)_5}\}_2]$ (X = Cl, Br) as is indicated by the decrease of the acute ring angles at the Sn atoms from 72·17 (2) and 71·91 (2)° in the Mn compounds to 69·89 (3)° in the title compound.

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* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39093 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The compound $[Re_2(CO)_8\{\mu\text{-}InRe(CO)_5\}_2]$, which contains a similar planar four-membered ring [Re—In—Re 71·07 (3)°, Re—Re 3·232 (1) Å] (Preut & Haupt, 1975), in which Sn is replaced by In, an atom of comparable size, has significantly larger acute ring angles at the In atoms and a longer Re—Re bond length across the ring. The variation of the homonuclear bond length and of the ring angle could be caused by the higher valence state of Sn compared with In in such clusters.

Both Sn atoms in the title compound are bonded to iodine and $Re(C_{18}H_{15}P)(CO)_4$ ligands. The ligand pairs are in the *trans* position with respect to the ring plane. The bond length Sn(1)—Re(2) is markedly shorter than the Sn—Re bond lengths in the ring and the bond lengths in $[SnBr_2\{Re(C_{18}H_{15}P)(CO)_4\}_2]$ [Sn—Re: 2·741 (2), 2·730 (2) Å] (Preut & Haupt, 1983). Such differences have not been observed between the Sn—Mn bonds in $[Mn_2(CO)_8\{\mu\text{-}Sn(X)Mn(CO)_5\}_2]$ (X = Cl, Br).

Intermolecular distances do not indicate interactions exceeding van der Waals forces.

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Dimeric *tert*-Butoxymagnesium Bromide–Diethyl Ether Adduct,* $[Mg_2Br_2(C_4H_9O)_2(C_4H_{10}O)_2]$: the Addition Product of a Grignard Reagent with Acetone

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Abstract. M_r = 502·9, monoclinic, $P2_1/c$, a = 9·68 (2), b = 11·10 (2), c = 15·10 (2) Å, β = 129·1 (2)°, U = 1259·1 Å^3, Z = 2 (dimer units), D_m = 1·30 (2), D_x = 1·33 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 3·5 mm^{-1}, $F(000)$ = 520, T = 293 K. Final R is 0·0986 for 672 observed photographic data. The molecule is a dimer, as in solution, with a four-membered Mg_2O_2 ring linking the two halves of the dimer round a centre of symmetry. Whereas the Mg atoms are four-coordinate by virtue of the two short bridging *tert*-butoxy O atoms, a longer terminal ether O and a terminal Br atom, the two kinds of O atom are three-coordinate and trigonal, with the central O and its three neighbours lying very accurately in a plane. Thus there is some degree of d_π–p_π interaction between the metal and *tert*-butoxy O atoms.

Introduction. Though organic chemists often consider the Grignard reagent to behave as simply 'RMgX' and consider reaction mechanisms in terms of such a formulation, considerable effort has been devoted to the study of the true constitution of solutions of Grignard reagents and also to the kinetics and mechanism of their reactions with carbonyls (Ashby, 1980; Ashby & Yu, 1971). Crystallographic studies have shown that Grignard reagents RMgBr.2Et$_2$O (R = Et, Ph), isolated from diethyl ether solutions, contain monomeric units, with Mg in an approximately tetrahedral environment (Stucky & Rundle, 1964; Guggenberger & Rundle, 1968), but there is little information about the nature of the products of the reactions of Grignard reagents with ketones before the usual hydrolysis is performed. Only rarely have these products been isolated and such

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