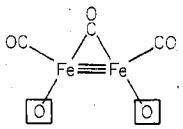

Multiply bonded carbonyl-bridged species have been studied by Ginley, Bock, and Wrighton.[21] Mechanistically a labile, multiply bonded, bridged dimeric iron species as the active catalytic intermediate is consistent with our photochemical data.

We have demonstrated that (1-pentene)$Fe(PF_3)_4$ has a PF_3 group that is photochemically active but that isomerization does not occur and that $Fe(PF_3)_5$ and $H_2Fe(PF_3)_4$ induce isomerization at elevated temperatures in the dark, but not photochemically. Thus we conclude that the higher PF_3-substituted iron carbonyls do not react by the Schroeder–Wrighton mechanism. Experimental evidence demonstrates the need for CO to generate photochemically a catalytically active species; we suggest that its function is formation of a bridged diiron species. A detailed mechanism for this process is proposesd elsewhere.[15]

Direct observation of a bridged species has been attempted. Analysis of reaction mixtures for a bridging carbonyl by infrared spectroscopy, however, is vitiated by the presence, in the spectral region of interest, of alkene bands which shift as the reaction proceeds. While the duration of the dark reaction following photolysis shows that the catalytic species has an adequate lifetime to be observed, failure to achieve its conclusive detection is likely due to its low concentration.

We plan to seek evidence for the carbonyl-bridged polynuclear species in a study of (olefin)$Fe(PF_3)_x(CO)_{4-x}$ compounds. A study of the chemistry of $Fe(PF_3)_x(CO)_{5-x}$ species in low-temperature matrices, a collaborative project with Turner and Poliakoff, has recently begun.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation (Grant CHE76-04006) for financial assistance.

Registry No. $Fe(CO)_5$, 13463-40-6; *ax*-$Fe(CO)_4PF_3$, 53368-95-9; *eq*-$Fe(CO)_4PF_3$, 35739-13-0; *trans*-$Fe(CO)_3(PF_3)_2$, 17594-22-8; *cis*-$Fe(CO)_3(PF_3)_2$, 17594-23-9; *vic*-$Fe(CO)_3(PF_3)_2$, 53275-22-2; *trans*-$Fe(CO)_2(PF_3)_3$, 17594-25-1; *cis*-$Fe(CO)_2(PF_3)_3$, 17594-26-2; *vic*-$Fe(CO)_2(PF_3)_3$, 53275-23-3; *eq*-$Fe(CO)(PF_3)_4$, 17594-29-5; *ax*-$Fe(CO)(PF_3)_4$, 17594-28-4; $Fe(PF_3)_5$, 13815-34-4; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; $H_2Fe(PF_3)_3CO$, 72883-57-9; $H_2Fe(PF_3)_4$, 31869-56-4.

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Contribution from the Departments of Chemistry, University of Maryland, College Park, Maryland 20742, and City of London Polytechnic, London EC3N 2EY, United Kingdom

Unsymmetrical Bis-Phosphorus Ligands. 13. Bis(*tert*-butylphosphino)(diphenylphosphino)methane and Some Derivatives[1]

Samuel O. Grim,*[2a-c] Patricia H. Smith,[2a,d] Ian J. Colquhoun,[2b] and William McFarlane[2b]

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Unsymmetrical bis(tertiary phosphine) ligands of the type $Ph_2PCH_2PR^1R^2$, where R^1 = Ph and R^2 = Me and *i*-Pr and where $R^1 = R^2$ = Me and *i*-Pr, along with the derivative compounds $Ph_2P(S)CH_2PR^1R^2$, $Ph_2P(S)CH_2P(S)PR^1R^2$, $[Ph_2PCH_2Pr^1R^2]M(CO)_4$, and $[Ph_2P(S)CH_2Pr^1R^2]M(CO)_4$, where M = Cr, Mo, or W, have been reported previously.[3,4] These compounds have proved interesting from the viewpoint of nuclear magnetic resonance (NMR) studies, especially with regard to phosphorus–phosphorus spin coupling and the phosphorus chelate shift effect.[5,6] The analogous compounds reported here, viz., $Ph_2PCH_2P(t\text{-}Bu)_2$ and its derivatives and $Ph_2P(S)CH_2P(s\text{-}Bu)_2$, extend and complement the previous studies.

The monosulfide, $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ was prepared in 43% purified yield from $Ph_2P(S)CH_2Li$[7] and $(t\text{-}Bu)_2PCl$ according to the reaction scheme shown by eq 1 and 2. In order to

$$Ph_3PS + CH_3Li \rightarrow Ph_2P(S)CH_2Li + C_6H_6 \quad (1)$$

$$(t\text{-}Bu)_2PCl + Ph_2P(S)CH_2Li \rightarrow Ph_2P(S)CH_2P(t\text{-}Bu)_2 + LiCl \quad (2)$$

reduce the extent of side reactions,[3] we placed phosphinous chloride in the reaction flask, and the lithium reagent was added dropwise. The disulfide $Ph_2P(S)CH_2P(S)(t\text{-}Bu)_2$ was prepared from the monosulfide by heating with elemental sulfur in benzene. The bis(tertiary phosphine) $Ph_2PCH_2P(t\text{-}Bu)_2$ was prepared as a viscous colorless oil in 75% yield from the monosulfide by reduction with Si_2Cl_6 in benzene. Quaternization of the monosulfide with methyl bromide produced the phosphonium salt $[Ph_2P(S)CH_2P(t\text{-}Bu)_2Me]Br$. Coordination reactions of the monosulfide to form a five-membered chelate ring and of the bis(tertiary phosphine) to form a four-membered chelate ring, by displacement of 2 CO's from $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, were carried out in a straightforward manner by direct reaction at ca. 100 °C. Apparently, the large steric bulk of the two *tert*-butyl groups of phosphorus did not materially affect its coordination ability, even when it was necessary to form a strained four-membered chelate ring. All of the types of reactions described above were also observed earlier with the methyl and isopropyl analogues.[3] However, the sulfur-transfer reaction (eq 3),[8] which is quite clean and can be used synthetically in the case of the methyl and isopropyl analogues, did not occur cleanly with $Ph_2P(S)CH_2P(t\text{-}Bu)_2$. Phosphorus-31 NMR evidence did indicate that some sulfur transfer had taken place with the *tert*-butyl compound, but the resulting reaction mixture was complex, and the products were not isolated or identified. It is likely that the steric effect of the *tert*-butyl groups plays an inhibitory role in this reaction.

$$Ph_2P(S)CH_2PR^1R^2 \xrightarrow{140\text{–}160\ ^\circ C} Ph_2PCH_2P(S)R^1R^2 \quad (3)$$

The synthesis of $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ led to a mixture of stereoisomers which exhibited three pairs of overlapping doublets in the ^{31}P NMR spectrum. Each diastereomer gives an AX spectrum with only a small degree of second-order character, i.e., a pair of doublets, the high-frequency doublet arising from P(V) in each case.

The ^{31}P NMR data are as follows: isomer A, $\delta(Ph_2PS)$ 42.0, $\delta(P(s\text{-}Bu)_2)$ −16.7, (J_{PP} = 78.7 Hz, relative intensity 0.43; isomer B, $\delta(Ph_2PS)$ 41.7, $\delta(P(s\text{-}Bu)_2)$ −15.9 (J_{PP} = 76.3,

* To whom correspondence should be addressed at the University of Maryland.

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Table I. ^{31}P NMR Data for $(C_6H_5)_2PCH_2PR_2$ Derivatives[a]

compd	R	$\delta(Ph_2P)$	$\delta(R_2P)$	$^2J_{PP}$	$\Delta(Ph_2P)$[b]	$\Delta(R_2P)$[b]
$Ph_2PCH_2PR_2$	Me	−22.8	−52.1	108		
	i-Pr	−19.9	−4.3	119		
	t-Bu	−16.0	16.2	138		
$Ph_2P(S)CH_2PR_2$	Me	39.0	−53.8	56	61.8	−1.7
	i-Pr	41.6	−9.3	77	61.5	−5.0
	s-Bu	42.0	−16.7	78.7		
	s-Bu	41.7	−15.9	76.3		
	s-Bu	42.2	−16.2	81.2		
	t-Bu	42.9	10.3	87	58.9	−5.9
$Ph_2P(S)CH_2P(S)R_2$	Me	32.4	35.3	17	55.2	87.4
	i-Pr	31.9	69.5	16	51.8	73.8
	t-Bu	37.8	73.4	16	53.8	57.2
$[Ph_2P(S)CH_2PR_2Me]Br$	Me	33.3	27.4	12	56.1	79.5
	i-Pr	33.4	44.2	14	53.3	48.5
	t-Bu	37.6	51.6	19.5	53.6	35.4
$[Ph_2PCH_2PR_2]Cr(CO)_4$	Me	25.8	5.4	35	48.6	57.5
	i-Pr	25.7	43.8	20	45.6	48.1
	t-Bu	26.6	61.5	12.5	42.6	45.3
$[Ph_2PCH_2PR_2]Mo(CO)_4$	Me	1.7	−24.8	8	24.5	27.3
	i-Pr	1.8	23.7	15	21.7	28.0
	t-Bu	2.8	43.0	22	18.8	26.8
$[Ph_2PCH_2PR_2]W(CO)_4$	Me	−23.4[c]	−53.5[d]	13	−0.6	−1.4
	i-Pr	−23.9[e]	1.1[d]	21	−4.0	5.4
	t-Bu	−22.0[f]	23.6[g]	25.6	−6.0	7.4
$[Ph_2P(S)CH_2PR_2]Cr(CO)_4$	Me	57.3	42.5	78	18.3	96.3
	i-Pr	57.9	82.3	70	16.3	91.6
	t-Bu	59.8	104.7	68.4	16.9	94.4
$[Ph_2P(S)CH_2PR_2]Mo(CO)_4$	Me	54.9	13.2	71	15.9	67.0
	i-Pr	55.5	60.5	64	13.9	69.8
	t-Bu	57.8	84.6	64.7	14.9	74.3
$[Ph_2P(S)CH_2PR_2]W(CO)_4$	Me	59.1	−4.2[h]	71	20.1	49.6
	i-Pr	60.2	49.0[i]	62	18.6	58.3
	t-Bu	62.2	76.2[j]	61	19.3	65.9

[a] δ values are in ppm; J values are in Hz. [b] The coordination shift is $\Delta = \delta$(complex) − δ(free ligand) or in the case of noncoordination compounds $\Delta = \delta$(compd) − $\delta(Ph_2PCH_2PR_2)$. [c] $J_{WP} = 199$ Hz. [d] $J_{WP} = 194$ Hz. [e] $J_{WP} = 203$ Hz. [f] $J_{WP} = 210$ Hz. [g] $J_{WP} = 190$ Hz. [h] $J_{WP} = 232$ Hz. [i] $J_{WP} = 227$ Hz. [j] $J_{WP} = 222$ Hz.

relative intensity 0.31); isomer C, $\delta(Ph_2PS)$ 42.2, $\delta(P(s\text{-}Bu)_2)$, −16.2 (J_{PP} = 81.2, relative intensity 0.26). The identification of the lines of each AX spectrum was facilitated by their different values of J_{PP} and by consideration of relative peak heights in spectra obtained in the absence of the NOE. However, no attempt was made to separate the diastereomers (the Fischer projections of which are given in Figure 1), and assignments of the isomers A, B, and C as particular diastereomers cannot be made except on the statistical grounds that the racemic modification may be assumed to be the isomer of greatest abundance, i.e, isomer A.

Phosphorus-31 NMR data for compounds with *tert*-butyl groups are reported in Table I, along with the previous data from the analogous methyl and isopropyl compounds. The chemical shifts of the dialkylphosphino groups in the bis(tertiary phosphines) and in the monosulfides follow the order expected from the group contributions[9] of organic groups in the chemical shifts in tertiary phosphine, viz., *t*-Bu > *i*-Pr > Me. This difference in group contribution is also reflected in a predictable way in all the other derivatives reported here. In the bis(tertiary phosphine) coordination compounds which contain a four-membered chelate ring, the ^{31}P coordination shift is slightly (2–3 ppm) less for the *t*-Bu compounds than for the *i*-Pr compounds. This difference has also been noted before in the case of monodentate tertiary phosphine complexes of the group 6 metal carbonyls, such as $LM(CO)_5$.[10,11] In the case of $[Ph_2PCH_2P(t\text{-}Bu)_2]W(CO)_4$, the coordination shift of the Ph_2P group is −6.0 ppm compared to +7.4 ppm for the $t\text{-}Bu_2P$ group. This 13.4-ppm difference between the two donor atoms in the tungsten compound compared to differences of 8.0 and 2.7 ppm in the molybdenum and chromium compounds, respectively, probably is a result of the larger atomic number of the tungsten atom, especially compared to the chromium atom, which permits the bulky $t\text{-}Bu_2P$ group to be more firmly bonded to the larger atoms.

In the coordination compounds $[Ph_2P(S)CH_2P(t\text{-}Bu)_2]M(CO)_4$ of the monosulfide ligands with the group 6 metal carbonyls, the five-membered chelate ring results in the un-

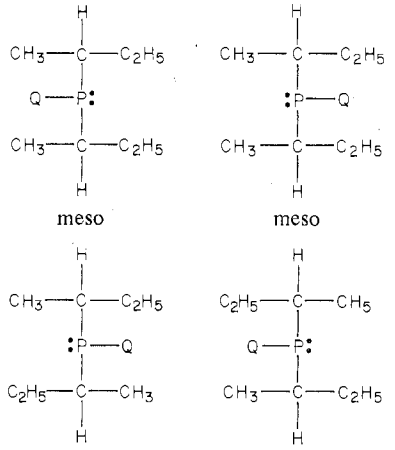

Figure 1. The stereoisomers of $(C_6H_5)_2P(S)CH_2P(s\text{-}C_4H_9)_2$.

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usually large, but expected,[12,13] ^{31}P coordination shift, known as the chelate ring effect,[5] of the phosphino phosphorus.[14] These coordination shifts are in the previously observed order Cr (94.4 ppm) > Mo (74.3) > W (65.9). Neither are the thiophosphoryl phosphorus coordination shifts especially large nor are they in the same order, but they have a minimum at molybdenum: Cr, 16.9; Mo, 14.9; W, 19.3 ppm. This order has also been observed with the analogous compounds.[3] The low value for the molybdenum compound may be related to a weaker sulfur–metal coordinate bond than for the other two metal complexes, since independently we have observed that the molybdenum carbonyl complexes of these monosulfide ligands decompose more rapidly in solution than do the chromium and tungsten analogues.

For the sequence of groups R = Me, *i*-Pr, and *t*-Bu the magnitude of J_{PP} increases in both the bis(tertiary phosphines) $Ph_2PCH_2PR_2$ (108, 119, 138 Hz) themselves and in the monosulfides $Ph_2P(S)CH_2PR_2$ (56, 77, 87 Hz). The differences in effective electronegativity of these alkyl groups are insufficient to produce changes of this size, and another possible explanation of this effect is that is arises from changes in the phosphorus hybridization due to the different steric requirements of Me, *t*-Pr, and *t*-Bu. The bulkier groups will tend to increase the CPC interbond angles and thus direct s character from the lone pair into the P–C bonds, including that to a bridging methylene group, and hence will increase the magnitude of couplings (including J_{PP}) which involve this P–C bond in the coupling path. However, it may be doubted whether the changes in phosphorus hybridization will be large enough to produce variations in the coupling constants that are as large as those actually observed. This is reinforced by the observations that in $[Ph_2PCH_2Pr_2]W(CO)_5$ the coupling $^1J(^{183}W^{31}P)$ is relatively insensitive to the bulk of R when this is alkyl, and there are significant differences in the values of J_{PP} in the diastereomers of $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ in all of which the P(III) hybridization can be assumed to be same. The remaining possibility is that the differences in J_{PP} arise from variations in the conformer populations in different molecules according to the bulk of the substituents on phosphorus. It is well established[15–17] that $^2J_{PP}$ is very sensitive to the relative lone pair/lone pair or lone pair/P:S orientations in many types of compound, and since in the present species the observed $^2J_{PP}$ is a weighted average over several different conformations, relatively small changes in the populations could produce quite large changes in J_{PP}. This is qualitatively confirmed by the inspection of scale molecular models from which it is clear that, when there are bulky groups on phosphorus, certain conformations will be significantly destabilized and will make correspondingly reduced contributions to the observed coupling constant. In this case of the chelate metal complexes the situation is complicated by the availability of two coupling paths which may well contribute additively to the observed coupling constant.

The phosphorus-31–tungsten-183 coupling constants in $[Ph_2PCH_2P(t\text{-}Bu)_2]W(CO)_4$ are 210 (Ph_2P) and 190 Hz((t-$Bu)_2P$), which are similar to the values in the analogous *i*-Pr and Me compounds. In each case, the magnitude J_{W-P} for the diphenylphosphino group is larger than that of the dialkylphosphino group. This observation has been discussed previously.[10,18] $^1J_{W-P}$ for the directly bound dialkylphosphino groups is noticeably larger (average of 227 Hz for three compounds) in the five-membered chelate rings than in the corresponding four-membered chelate rings (average of 193 Hz for three compounds) of the bis(tertiary phosphines).

Table II. Methylene Proton NMR Data for $Ph_2PCH_2PR_2$ Derivatives[a]

compd	R	$\delta(CH_2)$	$^2J_{Ph_2PCH}$	$^2J_{R_2PCH}$
$Ph_2PCH_2PR_2$	Me	2.12 s	~0	0
	i-Pr	2.07 d	~0	2.1
	t-Bu	2.00 d	~0	2.0
$Ph_2P(S)CH_2PR_2$	Me	2.64 d	13.0	0
	i-Pr	2.54 dd	13.0	1.9
	t-Bu	2.55 dd	12.5	2.0
$Ph_2P(S)CH_2P(S)R_2$	Me	3.45 dd	12.5	15.0
	i-Pr	3.31 dd	12.2	13.8
	t-Bu	3.22 dd	15.2	9.8
$[Ph_2PCH_2PR_2]Cr(CO)_4$	Me	3.76 t	9.5	9.5
	i-Pr	3.64 dd	9.6	8.3
	t-Bu	3.61 dd	9.6	7.6
$[Ph_2PCH_2PR_2]Mo(CO)_4$	Me	3.77 t	8.8	8.8
	i-Pr	3.69 dd	9.0	7.8
	t-Bu	3.66 dd	9.1	7.1
$[Ph_2PCH_2PR_2]W(CO)_4$	Me	4.24 t	9.1	9.1
	i-Pr	4.13 dd	9.0	8.0
	t-Bu	3.74 dd	9.0	7.0
$[Ph_2P(S)CH_2PR_2]Cr(CO)_4$	Me	2.98 dd	10.1	7.7
	i-Pr	2.87 dd	10.5	7.6
	t-Bu	2.85 dd	10.4	6.0
$[Ph_2P(S)CH_2PR_2]Mo(CO)_4$	Me	2.94 dd	10.4	7.7
	i-Pr	2.83 dd	10.6	6.8
	t-Bu	2.81 dd	10.5	5.8
$[Ph_2P(S)CH_2PR_2]W(CO)_4$	Me	3.01 dd	10.2	8.0
	i-Pr	2.99 dd	10.6	7.0
	t-Bu	2.87 dd	10.3	6.4
$[Ph_2P(S)CH_2PR_2Me]Br$	Me	4.69 dd	12.6	16.4
	i-Pr	4.60 dd	13.4	14.8
	t-Bu	3.96 t	12.5	12.5

[a] δ values are in ppm; J values are in Hz.

Proton NMR data are recorded in the Experimental Section and in Table II. For several of the compounds, such as $Ph_2P(S)CH_2P(S)(t\text{-}Bu)_2$ and $[Ph_2P(S)CH_2P(t\text{-}Bu)_2]Cr(CO)_4$, selective phosphorus double-irradiation experiments were performed in order to unequivocally assign the two $^2J_{PCH}$ values for the methylene protons, which in the absence of phosphorus decoupling are doublets of doublets. The remainder of the coupling constants were then assigned by their similarity with those in related compounds. It should be noted (Table II) that in the disulfides $Ph_2P(S)CH_2P(S)R_2$, the quaternary phosphonium salts $[Ph_2P(S)CH_2PR_2Me]Br$, and all the chelate compounds $[Ph_2P(S)CH_2PR_2]M(CO)_4$ and $[Ph_2PCH_2PR_2]M(CO)_4$, $^2J_{R_2PCH}$ decreases in magnitude for R in the order Me > *i*-Pr > *t*-Bu.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Microanalyses were performed by Dr. Franz Kasler, University of Maryland, and by Mr. Barry Saunderson, City of London Polytechnic. Proton NMR measurements were made on $CDCl_3$ solutions of the sample and tetramethylsilane as an internal reference with a Varian XL100 or JEOL FX60 NMR spectrometer. Phosphorus-31 data were obtained on the same instruments at 40.5 and 24.4 MHz, respectively, on CH_2Cl_2 solutions in 10-mm tubes. The ^{31}P chemical shifts are referenced to 85% H_3PO_4 and are reported as positive if at higher frequency than the reference.

$(C_2H_5)_2P(S)CH_2P(t\text{-}C_4H_9)_2$. This compound was prepared similarly to the previously reported isopropyl analogue by the addition of $(C_6H_5)_2P(S)CH_2Li$ (made from 26.5 g of Ph_3PS and 75 mL of 1.2 M MeLi in Et_2O–THF under N_2) to 17.9 g of t-Bu_2PCl in 100

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mL of Et_2O over a period of 3 h. To the residue, after stripping of the solvents, was added 150 mL of CH_2Cl_2. This mixture was extracted with H_2O to remove the salts, and then the solvents were removed again by rotary evaporation. Addition of 100 mL of EtOH to the resulting oil, stirring, and cooling furnished 14.6 g (43% yield) of colorless crystals, mp 159–161 °C. Anal. Calcd for $C_{21}H_{30}P_2S$: C, 67.00; H, 8.03; P, 16.45. Found: C, 67.41; H, 8.13; P, 16.70. Proton NMR: δ(Ph) 7.2–8.2 (m); $\delta(CH_2)$ 2.55 (dd, $^2J_{P(S)CH}$ = 12.5 Hz, $^2J_{PCH}$ = 2 Hz); $\delta(CH_3)$ 1.04 (d, $^3J_{PCCH}$ = 11.0 Hz).

$(C_6H_5)_2PCH_2P(t\text{-}C_4H_9)_2$. Reduction of $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ (3.2 g, 8.5 mmol) with excess Si_2Cl_6 (4.5 g) in 20 mL of refluxing C_6H_6 for 5 h produced, after slow hydrolysis at 0 °C with 27 mL of 30% aqueous NaOH and subsequent washing of the benzene layer and removal of the solvents, a colorless oily product in 75% yield. Proton NMR: δ(Ph) 7.0–7.6 (m); $\delta(CH_2)$ 1.99 (d, $^2J_{P(t\text{-}Bu_2)CH}$ = 2.0 Hz); $\delta(CH_3)$ 1.02 (d, $^3J_{PCCH}$ = 11.0 Hz).

$(C_6H_5)_2P(S)CH_2P(S)(t\text{-}C_4H_9)_2$. Addition of elemental S_8 (0.086 g) to 1.0 g of $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ in 30 mL of refluxing benzene for 4 h produced the disulfide product, which was obtained as colorless crystals (mp 162–164 °C) in 62% yield after removal of the solvent, addition of 25 ml of EtOH, and cooling. Anal. Calcd for $C_{21}H_{30}P_2S_2$: C, 61.74; H, 7.40; P, 15.16. Found: C, 61.48; H, 7.55; P, 15.40. Proton NMR: δ(Ph) 7.2–8.3 (m); $\delta(CH_2)$ 3.22 (dd, $^2J_{Ph_2P(S)CH}$ = 15.2 Hz, $^2J_{t\text{-}Bu_2P(S)CH}$ = 9.8 Hz); $\delta(CH_3)$ 1.32 (d, $^3J_{P(S)CCH}$ = 14.5 Hz).

$[(C_6H_5)_2P(S)CH_2P(t\text{-}C_4H_9)_2CH_3]Br$. Quaternization of $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ (1.0 g) was carried out with 5 mL of MeBr in 50 mL of C_6H_6 in a pressure bottle at room temperature for 12 h. The white precipitate (73% yield) was removed by filtration and washed with pentane. The salt (mp 230–231 °C) retains benzene of recrystallization quite tenaciously. Drying at refluxing toluene temperature for 24 h at 10^{-3} mmHg produced the solvent-free compound. Anal. Calcd for $C_{22}H_{33}P_2S$: C, 56.05; H, 7.06; P, 13.14; Br, 16.95. Found: C, 55.96; H, 7.14; P, 13.09; Br, 16.74. Proton NMR: δ(Ph) 7.2–7.6, 8.1–8.6 (m); $\delta(CH_2)$ 3.94 (t, $^2J_{P(S)CH} \approx {}^2J_{P(+)CH}$ = 12.5 Hz); δ(P–CH_3) 2.18 (d, $^2J_{PCH}$ = 11.5 Hz); δ(C–CH_3) 1.44 (d, $^3J_{PCCH}$ = 16 Hz).

$[(C_6H_5)_2PCH_2P(t\text{-}C_4H_9)_2]Cr(CO)_4$. Direct reaction of the ligand (5.0 g, 14.5 mmol) with 3.5 g (16.0 mmol) of $Cr(CO)_6$ in 30 mL of diethylene glycol dimethyl ether (diglyme) under N_2 at a temperature of 110–125 °C proceeded until CO evolution ceased. Cooling to room temperature, addition of several milliliters of hexane, and further cooling at −10 °C overnight produced yellow crystals which were collected by filtration and washed with EtOH. Excess $Cr(CO)_6$ was removed by sublimation. The product (dec pt 175 °C) was produced in 76% yield. Anal. Calcd for $C_{25}H_{30}CrO_4P_2$: C, 59.06; H, 5.95; P, 12.18. Found: C, 58.86; H, 6.04; P, 12.17. Proton NMR: δ(Ph) 7.2–7.8 (m); $\delta(CH_2)$ 3.61 (dd, $^2J_{Ph_2PCH}$ = 9.6 Hz, $^2J_{t\text{-}Bu_2PCH}$ = 7.6 Hz); $\delta(CH_3)$ 1.27 (d, $^3J_{PCCH}$ = 13.3 Hz).

$[(C_6H_5)_2PCH_2P(t\text{-}C_4H_9)_2]Mo(CO)_4$, a yellow crystalline compound (dec pt 165 °C), was prepared in an analogous fashion at a temperature of 75–95 °C in 85% yield. Anal. Calcd for $C_{25}H_{30}MoO_4P_2$: C, 54.36; H, 5.47; P, 11.21. Found: C, 54.48; H, 5.55; P, 11.10. Proton NMR: δ(Ph) 7.2–7.8 (m); $\delta(CH_2)$ 3.66 (dd, $^2J_{Ph_2PCH}$ = 9.6 Hz, $^2J_{t\text{-}Bu_2PCH}$ = 7.1 Hz); $\delta(CH_3)$ 1.23 (d, $^3J_{PCCH}$ = 13.5 Hz).

$[(C_6H_5)_2PCH_2P(t\text{-}C_4H_9)_2]W(CO)_4$, a yellow compound (dec pt 170 °C), was prepared in the same manner at a temperature of 100–120 °C in 71% yield. Anal. Calcd for $C_{25}H_{30}O_4P_2W$: C, 46.90; H, 4.72; P, 9.67. Found: C, 46.97; H, 4.75; P, 9.48. Proton NMR: δ(Ph) 7.2–7.9 (m); $\delta(CH_2)$ 3.74 (dd, $^2J_{Ph_2PCH}$ = 9.0 Hz, $^2J_{t\text{-}Bu_2PCH}$ = 7.0 Hz); $\delta(CH_3)$ 1.21 (d, $^3J_{PCCH}$ = 14 Hz).

$[(C_6H_5)_2P(S)CH_2P(t\text{-}C_4H_9)_2]Cr(CO)_4$. The compound was prepared by the reaction of $Ph_2P(S)CH_2P(t\text{-}Bu)_2$ (0.50 g, 1.3 mmol) and 0.32 g (1.4 mmol) of $Cr(CO)_6$ in 10 mL of diglyme and 4 mL of methylcyclohexane at 100 °C for several hours. Addition of 3 mL of hexane and cooling at −10 °C for 24 h produced crystals, which were dissolved in 25 mL of CH_2Cl_2 eluted through a short neutral alumina column. After concentration of the solution, addition of hexane produced yellow crystals (dec pt 120 °C) in 51% yield. Anal. Calcd for $C_{25}H_{30}CrO_4P_2S$: C, 55.55; H, 5.59; P, 11.46. Found: C, 55.49; H, 5.59; P, 11.27. Proton NMR: δ(Ph) 7.1–8.0 (m); $\delta(CH_2)$ 2.85 (dd, $^2J_{P(S)CH}$ = 10.4 Hz, $^2J_{PCH}$ = 6 Hz); $\delta(CH_3)$ 1.34 (d, $^3J_{PCCH}$ = 13.0 Hz).

$[(C_6H_5)_2P(S)CH_2P(t\text{-}C_4H_9)_2]Mo(CO)_4$, a yellow solid (dec pt 125 °C), was prepared in 60% yield in a similar fashion. Anal. Calcd for $C_{25}H_{30}MoO_4P_2S$: C, 51.38; H, 5.17; P, 10.60. Found: C, 51.45; H, 5.15; P, 10.81. Proton NMR: δ(Ph) 7.2–8.0 (m); $\delta(CH_2)$ 2.81 (dd, $^2J_{P(S)CH}$ = 10.5 Hz, $^2J_{PCH}$ = 5.8 Hz); $\delta(CH_3)$ 1.32 (d, $^3J_{PCCH}$ = 13.0 Hz).

$[(C_6H_5)_2P(S)CH_2P(t\text{-}C_4H_9)_2]W(CO)_4$, a yellow crystalline substance (dec pt 145 °C), was prepared analogously in 83% yield. Anal. Calcd for $C_{25}H_{30}O_4P_2SW$: C, 44.66; H, 4.50; P, 9.20. Found: C, 44.63; H, 4.42; P, 9.11. Proton NMR: δ(Ph) 7.3–7.9 (m); $\delta(CH_2)$ 2.87 (dd, $^2J_{P(S)CH}$ = 10.3 Hz, $^2J_{PCH}$ = 6.4 Hz); $\delta(CH_3)$ 1.34 (d, $^3J_{PCCH}$ = 13.3 Hz).

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Registry No. $Ph_2PCH_2PMe_2$, 62263-64-3; $Ph_2PCH_2P(i\text{-}Pr)_2$, 62263-67-6; $Ph_2PCH_2P(t\text{-}Bu)_2$, 74512-04-2; $Ph_2P(S)CH_2PMe_2$, 23176-51-4; $Ph_2P(S)CH_2P(i\text{-}Pr)_2$, 54006-31-4; $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ (isomer A), 74512-05-3; $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ (isomer B), 74559-78-7; $Ph_2P(S)CH_2P(s\text{-}Bu)_2$ (isomer C), 74559-79-8; $Ph_2P(S)CH_2P(t\text{-}Bu)_2$, 74512-06-4; $Ph_2P(S)CH_2P(S)Me_2$, 38055-42-4; $Ph_2P(S)CH_2P(S)(i\text{-}Pr)_2$, 62264-49-7; $Ph_2P(S)CH_2P(S)(t\text{-}Bu)_2$, 74512-07-5; $[Ph_2P(S)CH_2PMe_3]Br$, 62264-42-0; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2Me]Br$, 62264-43-1; $[Ph_2P(S)CH_2P(t\text{-}Bu)_2Me]Br$, 74512-08-6; $[Ph_2PCH_2PMe_2]Cr(CO)_4$, 62264-03-3; $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$, 62264-12-4; $[Ph_2PCH_2P(t\text{-}Bu)_2]Cr(CO)_4$, 74525-14-7; $[Ph_2PCH_2PMe_2]Mo(CO)_4$, 62264-04-4; $[Ph_2PCH_2P(i\text{-}Pr)_2]Mo(CO)_4$, 62264-13-5; $[Ph_2PCH_2P(t\text{-}Bu)_2]Mo(CO)_4$, 74525-15-8; $[Ph_2PCH_2PMe_2]W(CO)_4$, 62264-05-5; $[Ph_2PCH_2P(i\text{-}Pr)_2]W(CO)_4$, 62264-14-6; $[Ph_2PCH_2P(t\text{-}Bu)_2]W(CO)_4$, 74525-16-9; $[Ph_2P(S)CH_2PMe_2]Cr(CO)_4$, 62264-20-4; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]Cr(CO)_4$, 62264-23-7; $[Ph_2P(S)CH_2P(t\text{-}Bu)_2]Cr(CO)_4$, 74525-17-0; $[Ph_2P(S)CH_2PMe_2]Mo(CO)_4$, 62264-19-1; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]Mo(CO)_4$, 62264-22-6; $[Ph_2P(S)CH_2P(t\text{-}Bu)_2]Mo(CO)_4$, 74525-18-1; $[Ph_2P(S)CH_2PMe_2]W(CO)_4$, 62264-18-0; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]W(CO)_4$, 62264-21-5; $[Ph_2P(S)CH_2P(t\text{-}Bu)_2]W(CO)_4$, 74525-19-2; $(C_6H_5)_2P(S)CH_2Li$, 52101-86-7; $t\text{-}Bu_2PCl$, 13716-10-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; S_8, 10544-50-0; MeBr, 74-83-9.

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Gold(III) Oxidation of Disulfides in Aqueous Solution

C. Frank Shaw III,* M. P. Cancro, P. L. Witkiewicz, and J. E. Eldridge

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Although the use of gold-based drugs, chrysotherapy, has been an important form of treatment for rheumatoid arthritis for over half a century, our knowledge of the reactions of gold(I) and gold(III) with biologically important ligands and compounds is very limited. The current state of the art has been recently reviewed, and gold–sulfur interactions are found to be a major factor in gold biochemistry.[1] Gold is administered as thiolates such as gold(I) thioglucose and gold sodium thiomalate, because gold(III) complexes are too toxic for medicinal use.[2,3] The oxidation of thiols to disulfides[2] and methionine to methionine *S*-oxide[4,5] are cited as sources of

* To whom correspondence should be addressed at the Department of Chemistry.

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