

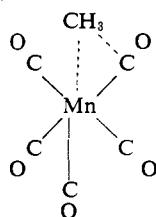
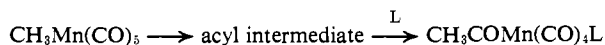
The Interaction of Phosphorus Ylides with Transition Metal Carbonyl Compounds. Triphenylphosphinemethylene and Bis(triphenylphosphine)carbon. Comparative Chemistry

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Abstract: Hexaphenylcarbodiphosphorane when treated with manganese pentacarbonyl bromide or rhenium pentacarbonyl bromide gives $M(\text{Br})(\text{CO})_4(\text{C}\equiv\text{CPPH}_3)$, $M = \text{Mn}$ or Re , and triphenylphosphine oxide. This is the first reported instance of a Wittig type reaction on a metal-coordinated carbonyl group. X-Ray diffraction studies show that an acetylide ligand is formed instead of the expected olefin. In contrast to this behavior, normal Wittig reagents give ylide carbene adducts with metal carbonyls of chromium, tungsten, and iron. These do not eliminate triphenylphosphine oxide under normal conditions. Rhenium pentacarbonyl bromide gives an ylide carbonyl adduct $\text{Re}(\text{CO})_5\text{CH}=\text{PPh}_3$, after transylidation.

One of the most common transformations in organometallic chemistry is the addition or insertion reaction since it includes an extensive list of carbon-metal bonded compounds and substrates which can undergo either intra- or intermolecular migration.² An often studied example of the ligand insertion is the intramolecular rearrangement of a methyl group in $\text{CH}_3\text{Mn}(\text{CO})_5$ upon interaction with the ligands ($L = \text{CO}$, $(\text{C}_6\text{H}_5)_3\text{P}$, $(\text{C}_6\text{H}_5\text{O})_3\text{P}$).³ The results of these studies are consistent with the postulate of an acyl intermediate as illustrated in the equation below.



This facile intramolecular addition can be extended to the synthesis of novel ligands by incorporating coordinatively unsaturated carbon ligands in the manganese pentacarbonyl moiety. Such a coordinatively unsaturated carbon ligand is bis(triphenylphosphine)-carbon or hexaphenylcarbodiphosphorane, $(\text{C}_6\text{H}_5)_3\text{P}=\text{C}^+\text{P}^-(\text{C}_6\text{H}_5)_3$,⁴ and triphenylphosphinemethylene, $(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$, whose reactions with transition metal complexes are compared in this paper.⁵

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(2) (a) R. F. Heck, *Advan. Chem. Ser.*, No. 49, 181 (1965); (b) R. F. Heck, *Accounts Chem. Res.*, 2, 10 (1969); (c) M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, 5, 225 (1967); (d) M. Green in "Transition Metals," Vol. 6, Part 2, M.T.P. International Review of Science, M. J. Mays, Ed., Butterworths, 1972, p 171; (e) A. Wojciki, *Advan. Organometal. Chem.*, 11, 87 (1973); (f) F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, 95, 3552 (1973).

(3) (a) A. Berry and T. L. Brown, *Inorg. Chem.*, 11, 1165 (1972), and references therein; (b) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, 7, 345 (1968); (c) F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, 1, 118 (1966); (d) C. P. Casey and C. A. Bunnell, *J. Amer. Chem. Soc.*, 93, 4077 (1971).

(4) (a) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, 83, 3539 (1961); (b) C. N. Matthews and G. H. Birum, *Accounts Chem. Res.*, 2, 373 (1969), and references therein.

(5) For a preliminary account of this work, see D. K. Mitchell, W. D. Korte, and W. C. Kaska, *J. Chem. Soc. D*, 1384 (1970); W. C. Kaska, D. K. Mitchell, and R. F. Reichelderfer, *J. Organometal. Chem.*, 47, 391 (1973).

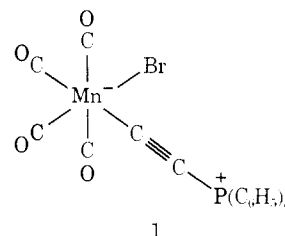
Results and Discussion

Manganese Pentacarbonyl Bromide and Hexaphenylcarbodiphosphorane. The interaction of $\text{Mn}(\text{CO})_5\text{Br}$ with $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{C}$ in benzene at 40° gives a yellow-orange viscous oil from which orange needles of $\text{Mn}(\text{Br})(\text{CO})_4\text{C}_2\text{PPh}_3$ (**1**) can be isolated after recrystallization.⁶ An equivalent quantity of triphenylphosphine oxide is isolated and identified by its mp $154\text{--}157^\circ$, ir $\gamma(\text{P}=\text{O})$ 1198 cm^{-1} , and mass spectrum, m/e 278, $(\text{C}_6\text{H}_5)_3\text{PO}^+$. A far infrared spectrum of **1** shows $\gamma(\text{MnBr})$ at 203 cm^{-1} compared to 218 cm^{-1} for $\gamma(\text{MnBr})$ in $\text{Mn}(\text{CO})_5\text{Br}$. Bands at 285, 292, and 300 cm^{-1} are assigned to $\gamma(\text{MnC})$. The carbonyl stretching region shows four bands at 2100 (w), 2010 (s), 1992 (s), and 1956 (w) cm^{-1} in CCl_4 solution. This is consistent with the cis form of $\text{Mn}(\text{CO})_4\text{L}_2$ complexes with C_{2v} local symmetry about the manganese atom in which the carbonyl groups should display four ir-active bands. Another band at 2105 cm^{-1} is tentatively assigned to the $\gamma(\text{C}\equiv\text{C})$, $(\text{C}_6\text{H}_5)_3\text{P}^+\text{C}\equiv\text{C}^-$, moiety in the complex.

The mass spectrum of **1** shows a molecular ion peak at m/e 533 followed by successive loss of CO groups and bromine to the ion m/e 341 $\text{MnC}_2\text{P}(\text{C}_6\text{H}_5)_3^+$.

The ^1H nmr spectrum of the complex at 60 MHz shows two peaks in the aromatic absorption region centered at $\delta_{\text{C}_6\text{D}_6}^{\text{MS}}$ 7.30 ppm with the ortho proton absorption of the triphenylphosphine group almost superimposed on those of the meta-para protons. Although the complex was diamagnetic according to magnetic susceptibility experiments, the ^1H absorptions of the triphenylphosphine group were broad and lacked fine structure.

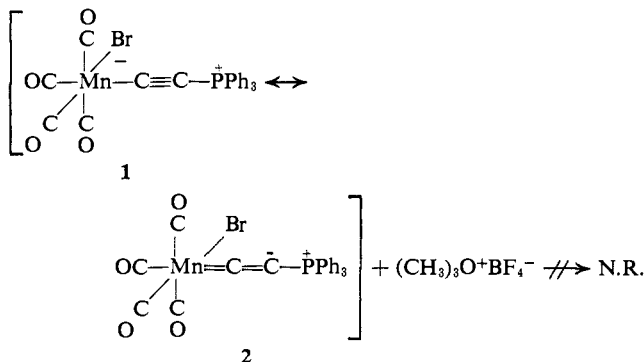
A recent X-ray crystal structure determination of **1** by Goldberg, Duesler, and Raymond⁶ is shown below.



(6) S. Z. Goldberg, E. N. Duesler, and K. Raymond, *Inorg. Chem.*, 11, 1397 (1972).

The complex contains a novel acetylide ligand with a C-C bond length of 1.216 Å, which is very similar to the normal acetylenic triple bond length of 1.204 Å. This manganese compound and the corresponding tungsten and rhenium complexes are the first reported instances of the neutral $(C_6H_5)_3P^+C\equiv C:^-$ ligand which can be considered as a triphenylphosphine complex of C_2 .⁷

Chemical Properties of $[Mn(Br)(CO)_4C_2PPh_3]$. The acetylide ligand $(C_6H_5)_3P^+C\equiv C:^-$ when coordinated to manganese is relatively unreactive toward air or water. Strong acids and alkylating agents such as trimethyl-oxonium fluoroborate do not form adducts. This indicates that resonance forms of the complex which emphasize canonical structure 2 with an ylidic α -

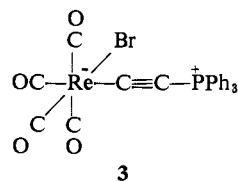


carbon atom are apparently not important. Bromine, however, does form a blue-green adduct with 1 in CCl_4 at 0° . Titration measurements show that only one molecule of bromine is absorbed by 1 to form the blue-green product, which slowly loses bromine at room temperature to give the original complex 1. The infrared spectrum of the bromine adduct which can be rapidly recorded in CCl_4 shows one $\gamma(C\equiv C)$ and four $\gamma(CO)$ stretching bands in the same position as observed for 1. The persistence of the $\gamma(C\equiv C)$ stretching vibration in the $(C_6H_5)_3P^+C\equiv C^-$ ligand complexed to manganese after treatment with bromine implies that addition to the triple bond has not occurred. This is very unusual for acetylenic compounds and it is clear that further experimental work is necessary to elucidate the chemistry of these highly polar forms of the acetylenic bond.^{8a,b}

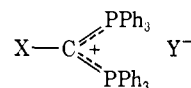
The precise nature of the adduct $MnBr_3(CO)_4(C\equiv CPh_3)$ is not immediately clear, although metal carbonyl trihalide complexes have been reported with coordination numbers higher than six.^{8c,d}

Rhenium Pentacarbonyl Bromide and Hexaphenylcarbodiphosphorane. Equimolar quantities of rhenium pentacarbonyl bromide and hexaphenylcarbodiphosphorane when heated in benzene at 76° for 18 hr give an off-white solid 3 after removal of solvent and recrystallization from methylene chloride and pentane. Triphenylphosphine oxide can be isolated from the crude reaction mixture and identified by comparison with an authentic sample. A 1H nmr spectrum of the air stable complex in chloroform-*d* shows an extremely broad resonance for the benzene ring protons on the

triphenylphosphine group. The peak is barely visible and is 240 Hz wide. A similar observation was noted when the nmr spectrum was recorded in benzene-*d*₆. The complex, however, can be quantitatively recovered unchanged from these solvents. It has the same melting point and $\gamma(CO)$ in CCl_4 solution. The complex is not paramagnetic according to esr or magnetic susceptibility experiments. A satisfactory explanation for the very broad 1H nmr spectrum is still lacking and must await further physicochemical experiments. The carbonyl stretching region shows four bands at 2113 (w), 1995 (s), 1985 (s), and 1932 (m) cm^{-1} in CCl_4 solution. This is consistent with C_{2v} local symmetry about the rhenium atom. The acetylenic band was assigned at 2024 cm^{-1} , although like complex 1 this is only a tentative assignment. An internal Wittig reaction similar to that proposed for the preparation of 1 can be postulated for the formation of 3.



Chemical Pathways with Phosphonium Ylides and Transition Metal Carbonyls. A. With Hexaphenylcarbodiphosphorane. The formation of 1 is the first reported instance of an apparent Wittig reaction by an ylide on a transition metal coordinated carbonyl group.^{5,9} Triphenylphosphine oxide, a typical Wittig reaction product, is isolated from the reaction mixture after treating $Mn(CO)_5Br$ with $(Ph_3P)_2C$. No evolution of carbon monoxide is observed during the reaction period. The precise manner by which $(Ph_3P)_2C$ interacts with $Mn(CO)_5Br$ is still not clear, although several possibilities can be presented. (1) A direct attack by $(Ph_3P)_2C$ on a metal coordinated carbon monoxide would yield an intermediate 4. The rapid loss of triphenylphosphine oxide from 4 would give the observed product 1. (2) A very common feature of hexaphenylcarbodiphosphorane chemistry is the tendency to form mesomeric species⁴ such as



where X = hydrogen, halogen, or as is possible in this case $M(CO)_5$, $M = Mn, Re$. The displacement of halide from group VII carbonyl halides has been reported to occur with some nucleophiles.^{2e,13} The coordinatively unsaturated carbodiphosphorane carbon atom in 5 can then attack the cis carbonyl group in an insertion reaction to give 4 which can lose triphenylphosphine oxide^{9,10} to form 1. These possibilities are shown in Scheme I.

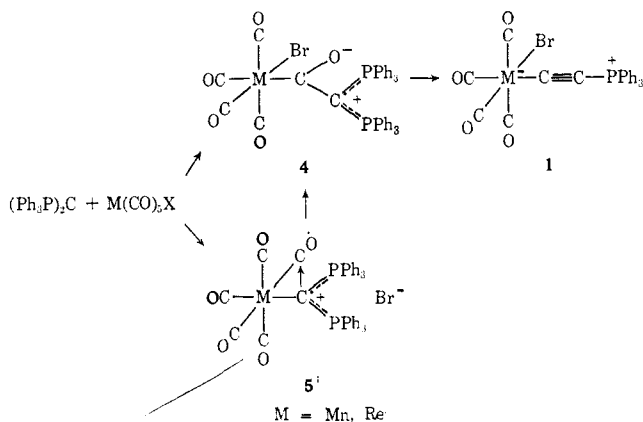
(9) Although the synthesis of 1 and 3 was performed in benzene, the possibility of other reaction products in polar solvents like THF cannot be excluded. The evolution of carbon monoxide was noted in several instances when $Mn(CO)_5Br$ was treated with $(Ph_3P)_2C$ in THF, although pure products could not be isolated. See also H. Alper and R. Partis, *J. Organometal. Chem.*, **44**, 371 (1972), who also report the isolation of Ph_3PO in the interaction of some Wittig ylides with iron carbonyls.

(10) Although the role of triphenylphosphine in Wittig reactions has been emphasized by H. Schlosser, *Colloq. Int. Cent. Nat. Rech. Scient.*, No. 182, 187 (1969), the particular role of triphenylphosphine in this reaction has not yet been delineated.

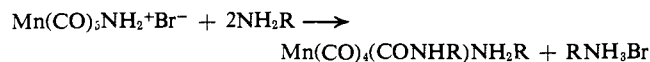
(7) P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Accounts Chem. Res.*, **6**, 97 (1973).

(8) (a) G. Modena and V. Tonellato, *Phys. Org. Chem.*, **9**, 185 (1971); (b) K. Yates, *et al.*, *J. Amer. Chem. Soc.*, **95**, 160 (1973); (c) M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 3494 (1965); (d) R. B. King, *Inorg. Chem.*, **3**, 1034 (1964).

Scheme I



There have been numerous examples of nucleophilic addition to metal coordinated carbonyl groups since the first report by Fischer and Maasböl.¹¹ Of particular importance here are the results of Angelici¹² and coworkers who have studied the interaction of group VII carbonyl complexes with primary amines. The resultant carboxamido complexes arise *via* nucleophilic attack on a cis carbonyl group by an amine



Other instances which involve direct attack of a nucleophile on group VII carbonyl complexes are the interaction of alkoxides with $\text{M}(\text{CO})_6^+$, $\text{M} = \text{Mn}$ or Re ,¹³ and direct attack of RLi to yield carbene complexes.¹¹ This mode of interaction of $(\text{Ph}_3\text{P})_2\text{C}$ with $\text{M}(\text{CO})_5\text{Br}$ ($\text{M} = \text{Mn}$ or Re) seems to be the most likely, although the generality of such Wittig type products from the direct attack of $(\text{Ph}_3\text{P})_2\text{C}$ on metal coordinated carbon monoxide is not completely evident. Treatment of $(\text{Ph}_3\text{P})_2\text{C}$ with other group VII metal carbonyl adducts such as $\text{Mn}(\text{CO})_5^+\text{BF}_4^-$, $\text{CF}_3\text{Mn}(\text{CO})_5$, and $h^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ in THF give either reduction or recovery of starting materials, respectively, with no indication of attack on the metal coordinated carbon monoxide. The treatment of chromium hexacarbonyl with $(\text{Ph}_3\text{P})_2\text{C}$ in refluxing THF or toluene gives displacement of carbon monoxide, although pure products could not be isolated, and no triphenylphosphine oxide can be detected in the reaction mixture. Tungsten hexacarbonyl, likewise, does not give characterizable products or triphenylphosphine oxide in refluxing THF or toluene. However, a product $\text{W}(\text{CO})_5\text{C}(\text{PPh}_3)_2$ can be isolated by treatment of $\text{W}(\text{CO})_6 \cdot \text{THF}$ with $(\text{Ph}_3\text{P})_2\text{C}$ in THF.⁵ Photochemical reactions of group VI carbonyls and $(\text{Ph}_3\text{P})_2\text{C}$ give complex products, and only one has been identified from the interaction of $\text{W}(\text{CO})_6$ with $(\text{Ph}_3\text{P})_2\text{C}$.⁵

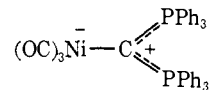
Treatment of diiron nonacarbonyl and $(\text{Ph}_3\text{P})_2\text{C}$ in benzene gives a dark brown insoluble, unstable product with the loss of one molecule of carbon monoxide.

(11) (a) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964); E. O. Fischer and R. Aumann, *Chem. Ber.*, **102**, 1495 (1961); (b) see reviews by F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); (c) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).

(12) R. J. Angelici, *Accounts Chem. Res.*, **5**, 335 (1972); R. W. Brink and R. J. Angelici, *Inorg. Chem.*, **12**, 1062 (1973).

(13) H. C. Lewis, Jr., and B. N. Storhoff, *J. Organometal. Chem.*, **43**, 1 (1973).

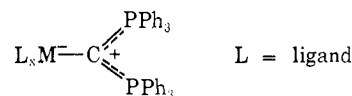
Nickel tetracarbonyl and $(\text{Ph}_3\text{P})_2\text{C}$ in refluxing diethyl ether gives a brick red monosubstitution product with the following probable structure.



The infrared spectrum (Nujol) in the carbonyl stretching region shows bands at 2015, 1978, and 1900 cm^{-1} . Other major bands in the ir spectrum are at 1190, 1100, 780, 750, 700, and 520 cm^{-1} .

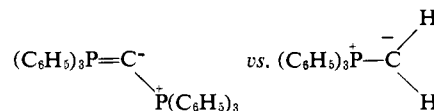
Thus all the thermal reactions of $(\text{Ph}_3\text{P})_2\text{C}$ with metal carbonyls except for Mn and Re complexes give substitution of the carbon monoxide rather than addition. Only one photochemical reaction has given the acetylenic ligand $\text{Ph}_3\text{P}+\text{C}\equiv\text{C}:-$.⁵

Theoretical calculations¹⁴ indicate that electron deficiency on the carbon atom in coordinated monoxide is the greatest among group VI metal carbonyls and group VII metal carbonyl cations and least in the group VIII metal carbonyls such as nickel. Hence it is not surprising that substitution of carbon monoxide gives the observed product with these later carbonyls. Nevertheless, it does seem unusual that a bent molecule such as hexaphenylcarbodiphosphorane¹⁵ with apparent ample opportunity for interaction by the coordinatively unsaturated carbon atom on other ligands will not readily add to a coordinated CO group in other metal carbonyls. On the other hand, the tendency to form mesomeric structures^{4,5} such as



which are common in the organic chemistry of hexaphenylcarbodiphosphorane, may indicate that coordinated ligands must come in extremely close proximity to the electron rich α -coordinatively unsaturated carbon atom before reaction can occur. Such a case would only be observed when hexaphenylcarbodiphosphorane is strongly bound to the metal surface.

B. With Triphenylphosphinemethylene. By comparison, the replacement of one triphenylphosphine group on hexaphenylcarbodiphosphorane with hydrogen atoms gives the familiar Wittig ylide, triphenylphosphinemethylene



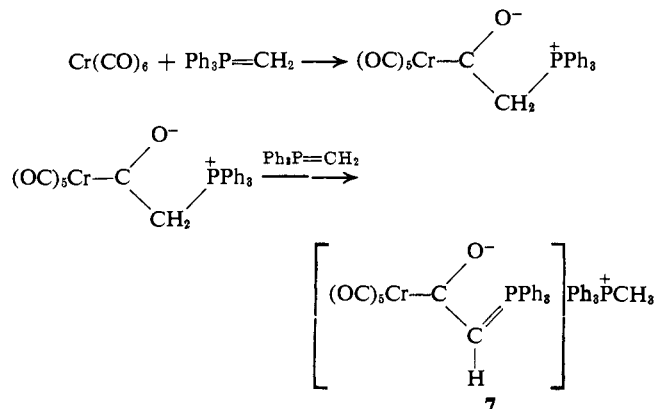
This molecule with transition metal carbonyl complexes shows a variety of substitution and addition reactions which in some respects contrast with hexaphenylcarbodiphosphorane. Wilke¹⁶ and coworkers have reported on the facile substitution of carbon monoxide in nickel carbonyl, and Fischer, *et al.*, have attested to the stability of the 1,3-dipolar form with a variety of metal

(14) (a) A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366 (1968); (b) D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968); (c) K. G. Caulton and R. F. Fenske, *ibid.*, **7**, 1273 (1968).

(15) A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 617 (1972).

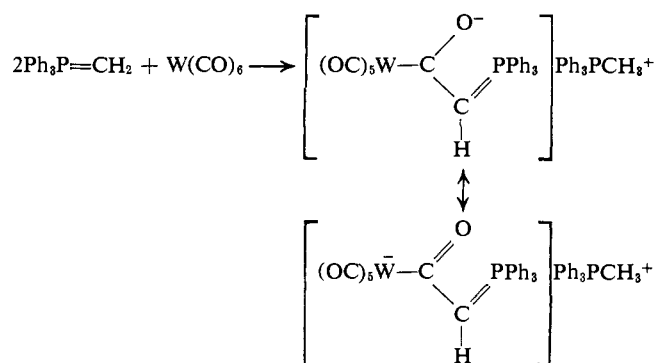
(16) F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E. G. Hoffmann, G. Schroth, K. Seevogel, and W. Stempfle, *Isr. J. Chem.*, **10**, 293 (1972).

the doublet at δ 3.05 as the methyl protons in the $\text{Ph}_3\text{PCH}_3^+$ species. A similar set of equations can describe the product obtained with the salt-free ylide.



With $\text{Ph}_3\text{PCH}_3^+$ as the cation, the ylidic proton always shows a $J_{\text{PCH}} = 40$ Hz in THF, pyridine, or $\text{DMSO}-d_6$. The ir spectrum of the ylide adduct in the carbonyl stretching region also supports the structure shown above. In THF solution the adduct shows four $\gamma(\text{CO})$ bands at 2015 (w), 1985 (m), 1890 (s), and 1859 (m) cm^{-1} . Ordinarily three ir active bands are observed for C_{4v} symmetry of pentacarbonyl adducts, although an infrared inactive band of B_1 symmetry can often become allowed if the symmetry of the complex is distorted from idealized C_{4v} symmetry. Although the peak at 1985 cm^{-1} occurs at the same frequency as $\text{Cr}(\text{CO})_6$, there was no evidence for $\text{Cr}(\text{CO})_6$ as an impurity. After five recrystallizations from THF-pentane, the 1985- cm^{-1} band shows no diminution in intensity. The presence of THF could, however, induce slight decomposition of the complex which has often been observed to be the case with carbene complexes.²⁰

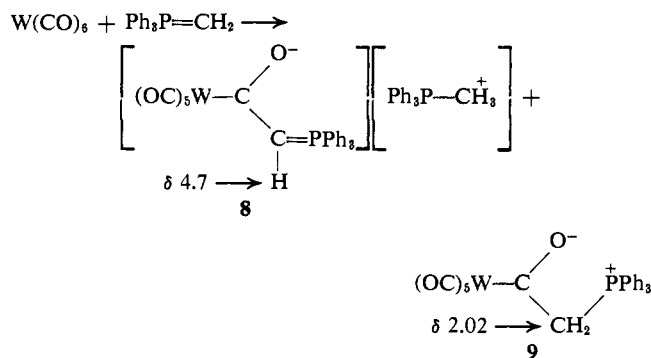
Tungsten hexacarbonyl and triphenylphosphinemethylene also give an addition product similar to that found for chromium hexacarbonyl when the reactants are mixed in a 1:2 molar ratio, respectively.



The interaction of both tungsten and chromium hexacarbonyl with triphenylphosphinemethylene in a 1:1 molar ratio, respectively, however, gives two products **8** (70%) and **9** (30%) as determined by nmr. An nmr spectrum of the product in cold pyridine shows a set of three doublets at $\delta_{\text{C}_6\text{H}_5\text{N}}^{\text{TMS}}$ 4.7 ppm, $J_{\text{PCH}} = 41.5$ Hz, $\delta_{\text{C}_6\text{H}_5\text{N}}^{\text{TMS}}$ 3.4 ppm, $J_{\text{PCH}} = 13.5$ Hz, and $\delta_{\text{C}_6\text{H}_5\text{N}}^{\text{TMS}}$ 2.0 ppm, $J_{\text{PCH}} = 13$ Hz, with a trace of proton absorptions from THF at δ 1.4 and 3.4 ppm. The low-field

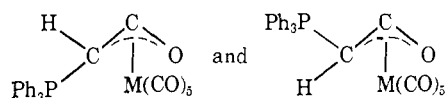
(20) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, **9**, 32 (1970).

doublets at δ 4.7 and 3.4 are in the ratio of 1:3, and the doublet at δ 2.0 is assigned to a nontransylidated complex. An infrared spectrum in the carbonyl stretching region shows bands at 2031 (vw), 1981 (m), 1894 (s), and 1861 (w) cm^{-1} with shoulders at 1912 and 1945 cm^{-1} . The following equation best describes these results.

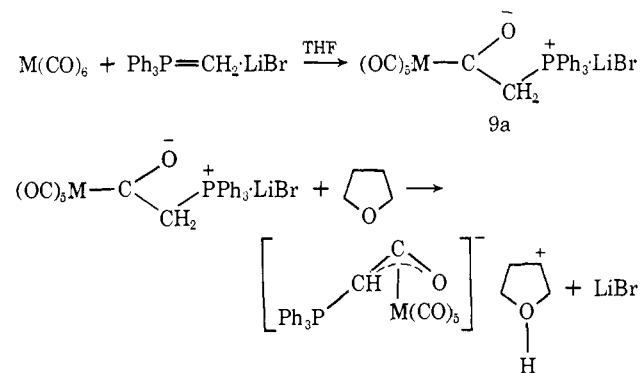


These results with the group VI transition metal carbonyls are in sharp contrast to those reported by tom Dieck, Starzewski, Franz, and Hohman^{17b} in which only substitution of the metal coordinated carbon monoxide was observed. In no case did we observe substitution products with salt-free ylide and group VI transition metal carbonyls in ether, THF, or benzene solvents.

A more recent report by Greco^{17c} ascertains that 1:1 adducts of the types



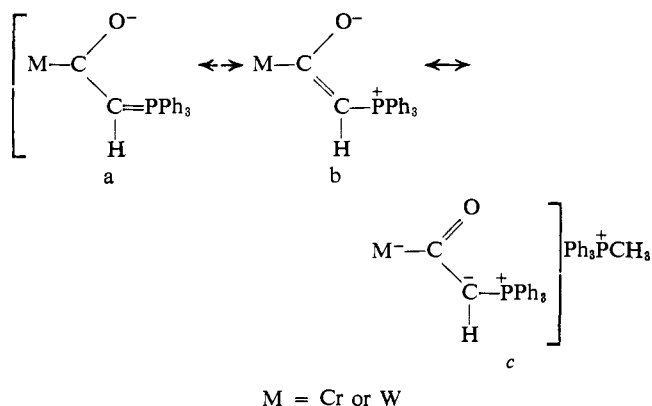
were obtained upon interaction of $\text{Ph}_3\text{P}=\text{CH}_2 \cdot \text{LiBr}$ generated *in situ* with group VI metal carbonyls instead of the 2:1 adducts reported here. A THF oxonium cation has been postulated as the counterion species in this complex. The following equation can describe the reaction postulated by Greco.^{17c}



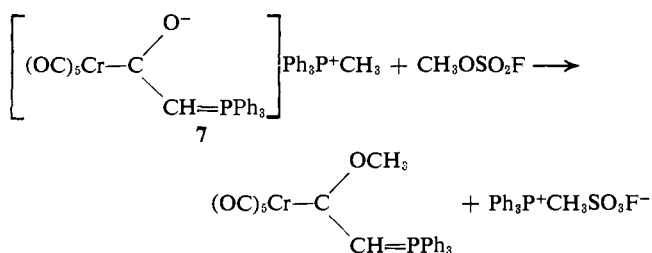
The approximate $\text{p}K_a$ of THF in water is -2.1 and the $\text{p}K_a$ of most conjugate acids of ylides range from 5 to 7. Even though these values reflect determinations in water, it does not seem likely that THF is a strong enough base to remove a proton from **9a** at equilibrium. The postulate of a π -allylic structure for the ylide pentacarbonyl complex is unnecessary since more than the requisite number of electrons are present for the next inert gas configuration if an allyl group is considered to be a three electron donor system.²¹

(21) R. B. King, "Transition Metal Organometallic Chemistry," Academic Press, New York, N. Y., 1969, p 4.

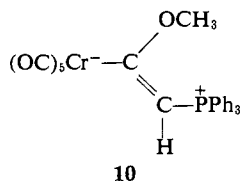
There are several resonance forms of the triphenylphosphinemethylene adduct of chromium and tungsten hexacarbonyl which are shown below.



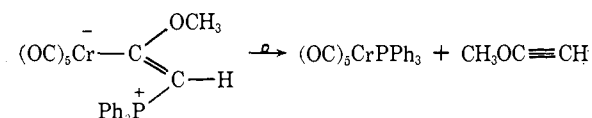
Form a represents a carbene structure which would alkylate to give a carbene-ylide complex. Form b would also alkylate on the oxygen atom, but a dipolar form would result, and the last form would suggest alkylation at carbon. With methyl fluorosulfonate as the alkylating agent, a precipitate of methyltriphenylphosphonium fluorosulfonate is obtained and a yellow benzene soluble complex whose ^1H nmr spectrum in benzene- d_6 shows a doublet at $\delta_{\text{C}_6\text{D}_6}^{\text{TMS}}$ 5.4, $J_{\text{PCH}} = 33$ Hz, and a singlet at $\delta_{\text{C}_6\text{D}_6}^{\text{TMS}}$ 3.5 in the ratio of 1:3, respectively. It is clear that methylation occurs on the oxygen atom according to the following equation.



The highly deshielded hydrogen atom, δ 5.4 ppm, α to the triphenylphosphine group suggests that the methylated complex could very well be described as shown in **10**. There is no evidence, however, that **10** undergoes a



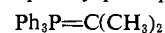
rearrangement to give alkoxy acetylene in a fashion postulated by Casey and Burkhardt²² in their vinyl ether synthesis.



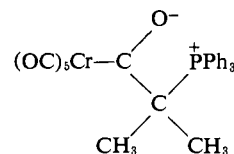
The infrared spectrum $\gamma(\text{CO})$ of the methylated complex in THF shows two bands at 2048 and 1924 cm^{-1} . Treatment of the methylated complex **10** with benzaldehyde did not give any evidence for Wittig reaction products.

(22) C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **94**, 6543 (1972).

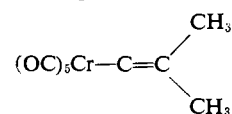
Since the only example of a Wittig reaction with metal coordinated carbon monoxide ligands is observed with hexaphenylcarbodiphosphorane (*vide infra*), the interaction of chromium and tungsten hexacarbonyls with isopropylidene-triphenylphosphorane was studied.



The blocking methyl groups would prevent transylidation and promote elimination of triphenylphosphine oxide from the intermediate betaine.



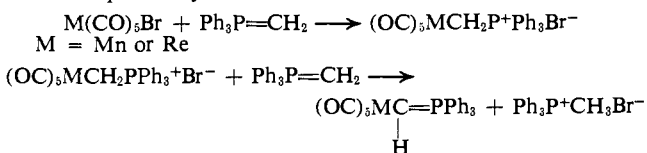
A very small amount of crystals could be isolated from the reaction mixture. These were identified as triphenylphosphine oxide by melting point, ir, and mass spectrum by comparison with authentic material, but no product which corresponded to



could be isolated from the reaction mixture.²³

With Manganese Pentacarbonyl Bromide and Rhenium Pentacarbonyl Bromide. The addition of alkali halide free methylenetriphenylphosphorane to manganese pentacarbonyl bromide in a 1:1 molar ratio in THF gives a white solid and an unidentifiable red oil after removal of THF. Dimanganese decacarbonyl sublimes from the reaction mixture. The white solid is identified as methyltriphenylphosphonium bromide. When the same reaction is performed with manganese pentacarbonyl bromide and methylenetriphenylphosphorane in a 1:2 molar ratio, respectively, a quantitative yield of methyltriphenylphosphonium bromide is obtained and a red oil which cannot be purified but gives dimanganese decacarbonyl under vacuum.

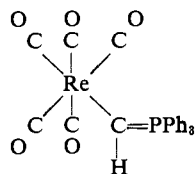
By using rhenium pentacarbonyl bromide and methylenetriphenylphosphorane in a 1:2 molar ratio, respectively, methyltriphenylphosphonium bromide is filtered from the reaction mixture. Removal of solvent gives a pale yellow solid with $\gamma(\text{CO})$ stretching bands in THF at 2078 (w), 1989 (s), and 1911 (*m*) cm^{-1} . A ^1H nmr spectrum of the rhenium complex in benzene- d_6 or dichloromethane shows a doublet at $\delta_{\text{C}_6\text{D}_6}^{\text{TMS}}$ 0.8 ppm, $J_{\text{PCH}} = 10$ Hz,²⁴ and aromatic hydrogen atoms at δ 7.4 ppm. These results can be interpreted by the following reaction pathway.



(23) Similar complexes have been prepared recently as cyano derivatives of metal carbonyls; cf. R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972).

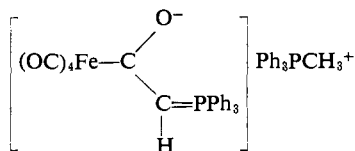
(24) The sample of rhenium complex must be very pure to observe the ylide proton doublet in the ^1H nmr. If traces of methyltriphenylphosphonium cation are present, the doublet is broadened and often times cannot be observed at all. The spectrum of the complex can be improved if a small amount of dry alumina is placed in the nmr tube with the sample; cf. H. J. Bestmann, H. G. Liberda, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 2963 (1968). W. C. K. thanks Professor Bestmann for pointing out this feature.

Other side reactions could occur when the central metal is manganese, but insertion reactions of rhenium complexes are rare^{26, 13} and hence isolation of



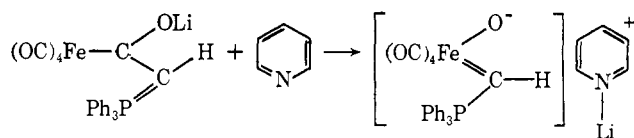
as a transition metal ylide adduct is possible. In neither case was triphenylphosphine oxide observed.

With Iron Pentacarbonyl. The generality of ylide addition to coordinated carbonyl groups can be extended to iron pentacarbonyl. Treatment of triphenylphosphinemethylene with iron pentacarbonyl in a 2:1 molar ratio respectively in benzene or ether gives an immediate yellow precipitate with no elimination of carbon monoxide. An infrared spectrum in the $\gamma(\text{CO})$ stretching region shows bands at 1988 (m), 1897 (sh), and 1884 (s) cm^{-1} . Peaks at similar positions have been observed for other iron tetracarbonyl adducts. The nmr spectrum of the yellow solid in pyridine shows a doublet at $\delta_{\text{C}_6\text{H}_5\text{N}}^{\text{TMS}}$ 4.00 ppm, $J_{\text{PCH}} = 39$ Hz, and $\delta_{\text{C}_6\text{H}_5\text{N}}^{\text{TMS}}$ 3.1 ppm, $J_{\text{PCH}} = 15$ Hz. The doublet peak at δ 4.00 is assigned to the methylene ylide proton, similar to that observed with chromium and tungsten carbonyl adducts, and the doublet peak at δ 3.1 ppm is assigned to the methyl group of the methyltriphenylphosphonium cation.



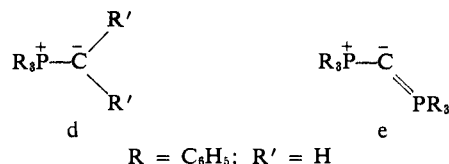
There is relatively little change in the chemical shift of the ylidic proton in $\text{DMSO}-d_6$, $\delta_{\text{DMSO}-d_6}^{\text{TMS}}$ 3.8 ppm, $J_{\text{PCH}} = 38$ Hz, compared to that observed in pyridine as a solvent. This supports the postulate that the methyltriphenylphosphonium cation is not as closely associated with the ylide carbene anion as an alkali metal cation would be.

To test this hypothesis further, iron pentacarbonyl in ether is treated with $\text{Ph}_3\text{P}=\text{CH}_2 \cdot \text{LiBr}$ in a 1:2 molar ratio, respectively. A white precipitate, $\text{Ph}_3\text{PCH}_3^+\text{Br}^-$, is obtained and a deep yellow solution. The yellow solution gives a red-brown solid after vacuum removal of the ether. A ^1H nmr spectrum of the red-brown solid in cold pyridine shows two sets of doublets, one at $\delta_{\text{C}_5\text{H}_5\text{N}}^{\text{TMS}}$ 5.1, $J_{\text{PCH}} = 38$ Hz, and $\delta_{\text{C}_5\text{H}_5\text{N}}^{\text{TMS}}$ 4.9, $J_{\text{PCH}} = 34$ Hz. The ratio of the doublets was 5:1, respectively. In contrast, the red solid in $\text{DMSO}-d_6$ shows only one peak at $\delta_{\text{DMSO}-d_6}^{\text{TMS}}$ 3.8, $J_{\text{PCH}} = 38$ Hz. As in the previous case with tungsten, the observation of different nmr data can be explained by postulating a preferential cationic solvation by pyridine to generate an ion pair in which the lithium cation is no longer held tightly to the ylide carbonyl.

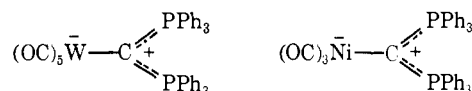


Summary

Phosphorus ylides d and e which are coordinatively unsaturated, 1,2-dipolar complexes of carbon have been compared in their reactivity with metal carbonyl compounds. Type d compounds add to metal coordinated



carbon monoxide and illustrate a novel aspect of transylidation to give ylide carbene complexes. In contrast, the addition of type e compounds to metal coordinated carbon monoxide is limited to manganese and rhenium carbonyl halides. These give Wittig reaction products which represent a hitherto unreported type of acetylenic ligand, $\text{Ph}_3\text{P}^+\text{C}\equiv\text{C}^-$. The other reactions of type e compounds include displacement of coordinated ligands to give compounds of the type



Experimental Section

Operations. All experiments with hexaphenylcarbodiphosphorane and transition metal complexes were performed under dry oxygen-free nitrogen or argon. The pure gas was transferred to all systems via Teflon lined flexible metal tubing of aircraft variety with ground joint connectors which could be attached to reaction flasks.

Infrared spectra were recorded on a Beckman IR-7 (prism grating) instrument which was calibrated in the 1700–2050- cm^{-1} region with polystyrene film and atmospheric water vapor, or a Perkin-Elmer 337 grating spectrometer. Mass spectra were recorded at 70 eV on a AEI MS-9 instrument. Molecular weight measurements were made with a cryoscopy cell designed by Dilts and Shriver.²⁵

Nmr spectra were recorded on a Varian HA 100 or T-60 instrument which operated at 37°. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratories, 56-19 37th Avenue, Woodside, N.Y. 11377, and Alfred Bernhardt, Fritz-Pregel Strasse 14-16, 5251 Elbach über Engels Kirchen, West Germany.

Materials. Hexaphenylcarbodiphosphorane was synthesized by the method of Ramirez, *et al.*⁴ Metal carbonyl complexes were obtained from Pressure Chemical Co., 3419-25 Smallman Street, Pittsburg, Pa. 15201, and were sublimed before use. Triphenylphosphinemethylene was recrystallized three times from hexane.²⁶ Tetrahydrofuran was distilled from lithium aluminum hydride or sodium benzophenone ketyl immediately before use. Dichloromethane, benzene, and hexane were distilled from lithium aluminum hydride or sodium bis(2-methoxyethoxy)aluminum hydride.

A. Manganese Pentacarbonyl Bromide and Hexaphenylcarbodiphosphorane. Hexaphenylcarbodiphosphorane (1.0 g, 3.64 mmol) dissolved in 40 ml of benzene was added to a suspension of manganese pentacarbonyl bromide in 15 ml of benzene over a period of 1 hr at room temperature. The manganese pentacarbonyl bromide slowly dissolved to give a deep red-orange solution which was heated to 35–40° for 12 hr. Filtration and removal of solvent gave a red-orange oil which was recrystallized from methylene chloride and pentane, according to the following method. The oil was dissolved in a minimum of methylene chloride and enough pentane added to induce formation of a red oil. The liquor was separated from the red oil into another flask and more pentane was added until no further red oil separated. The liquors were then cooled to 0° and fine yellow-orange needles formed. More pentane or hexane can be added to the liquors to induce further crystallization. The yellow-orange needles, mp 128–129°, 1.0 g

(25) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 161.

(26) R. Köster, D. Simic, and M. A. Grassberger, *Justus Liebig's Ann. Chem.*, **739**, 211 (1970).

(51.9%), are moderately stable in air, although benzene solutions eventually become brown.

Anal. Calcd for $C_{24}H_{16}O_4PMnBr$: C, 54.06; H, 2.84; P, 5.81; Br, 14.99; mol wt 533. Found: C, 54.32; H, 3.01; P, 5.61; Br, 14.92; mol wt 503.

B. Rhenium Pentacarbonyl Bromide and Hexaphenylcarbodi-phosphorane. Hexaphenylcarbodi-phosphorane (0.53 g, 0.98 mmol) and rhenium pentacarbonyl bromide (0.4 g, 0.98 mmol) were dissolved in 40 ml of benzene and heated at 76° for 18 hr. The pale yellow solution was filtered from a small amount of gummy residue and the solvent removed to give an off-white oily solid. The material was recrystallized from methylene chloride and pentane to give 0.3 g (46%) of white needles, mp 143–145°. Slow evaporation of a methylene chloride–pentane solution of the adduct gives long feathery white needles which are stable in air.

Anal. Calcd for $C_{24}H_{16}O_4PReBr$: C, 43.37; H, 2.28; Br, 12.03; P, 4.66. Found: C, 43.46; H, 2.55; Br, 12.78; P, 4.68.

C. The Interaction of Hexaphenylcarbodi-phosphorane and Nickel Tetracarbonyl. Nickel tetracarbonyl (0.35 g, 0.27 ml, 2.06 mmol) in 5 ml of ether was slowly added to hexaphenylcarbodi-phosphorane (1.1 g, 2.06 mmol) in 300 ml of refluxing ether. The solution became deep red orange and a brick red solid formed. The solution was refluxed for 2.5 hr whereupon the ether was decanted from the red adduct. The compound was washed with fresh ether to give 1.3 g (93%) of an air sensitive brick red complex which was slightly soluble in benzene, ether, and THF, mp 160° dec.

Anal. Calcd for $C_{40}H_{30}P_2O_3Ni$: C, 70.72; H, 4.45; P, 9.12; O, 7.07. Found: C, 70.52; H, 4.71; P, 9.40; O, 7.35.

D. The Interaction of Bromine with 1. A solution of **1** (0.2 g, 0.375 mmol) in 20 ml of carbon tetrachloride was treated with bromine (0.06 g, 0.024 ml, 0.375 mmol) in carbon tetrachloride at room temperature. The bromine color was immediately discharged and a deep blue-green solid was deposited. Excess carbon tetrachloride was decanted from the blue solid. Under vacuum **3** slowly becomes yellow and **1** can be isolated and identified by melting point and infrared spectrum. Deep blue-green solutions of **3** were formed with dry, freshly distilled methylene chloride or dichloroethane. Blue-green solutions also formed in acetone and acetonitrile which immediately turned yellow in air.

E. The Interaction of Triphenylphosphinemethylene with Chromium Hexacarbonyl. $[Ph_3PCH_2]^+[Cr(CO)_6C(O)CHPh_3]^-$. A solution of triphenylphosphinemethylene (1.5 g, 5.45 mmol) in 20 ml of THF was slowly added to a stirred solution of chromium hexacarbonyl (0.60 g, 2.73 mmol) in 40 ml of THF at 24°. The orange solution was stirred for 4.5 hr whereupon the THF was removed under vacuum to give a bright yellow solid. This material can be crystallized by adding a minimum of THF followed by the addition of pentane or hexane until the solution becomes cloudy. This cloudy solution when allowed to cool in an ice bath gave yellow needles, 1.5 g (69.5%), mp 115–126°.

Anal. Calcd for $C_{44}H_{34}O_6P_2Cr$: C, 68.40; H, 4.43; O, 12.43; P, 8.01. Found: C, 68.17; H, 4.59; P, 7.79; O, 12.40.

F. The Interaction of Triphenylphosphinemethylene–Lithium Bromide Complex with Tungsten Hexacarbonyl. A solution of triphenylphosphinemethylene–lithium bromide complex in THF (8.7 mmol) was slowly added to a THF solution of tungsten hexacarbonyl (1.53 g, 4.35 mmol) in THF. A precipitate of methyltriphenylphosphonium bromide formed immediately. After 4 hr the solution was filtered and excess THF was removed under vacuum. If all of the THF is removed, the yellow complex **6** becomes partially red-brown and gummy. This red-brown material could be washed with fresh, cold THF to give bright yellow **6**.

G. The Interaction of Methylene-triphenylphosphorane with Tungsten Hexacarbonyl. $[Ph_3PCH_2]^+[W(CO)_6C(O)CHPh_3]^-$. A solution of methylene-triphenylphosphorane (1.0 g, 3.63 mmol) in 20 ml of THF was slowly added to a stirred solution of tungsten hexacarbonyl (0.64 g, 1.81 mmol) in 40 ml of THF at 24°. The yellow solution was stirred for 4 hr whereupon removal of THF gave a bright yellow solid. The yellow solid was redissolved in 10–15 ml of THF and filtered and hexane added until the solution

became cloudy. When this mixture was cooled in an ice bath, yellow crystals of product appeared, 0.95 g (65%), mp 127–132°.

H. The Preparation of $(CO)_6CrCH_2PPh_3$. A solution of methylene-triphenylphosphorane (1.0 g, 3.63 mmol) in 15 ml of THF was added dropwise to a stirred solution of triphenylphosphine-pentacarbonylchromium in 30 ml of THF at 24°. After stirring for 27 hr, the THF was removed to give an oily orange solid which was recrystallized from toluene and pentane. Repeated recrystallizations from toluene and pentane gave yellow crystals, mp 125.5–131.5, no decomposition. The $\nu(CO)$ stretching region showed bands at 2048 (w), 1882 (m), and 1918 (s) cm^{-1} . The 1H nmr spectrum in benzene- d_6 showed a multiplet of bands $\delta_{C_6D_6}^{TMS}$ 7.10 ppm for the benzene ring protons and a doublet $\delta_{C_6D_6}^{TMS}$ 0.6, $J_{PCH} = 14$ Hz, for the ylide proton.

I. The Alkylation of the Chromium Carbonyl Adduct 7. Freshly distilled methyl fluorosulfonate (Magic Methyl) (0.059 g, $d = 1.4$ g/ml), 0.52 mmol in 10 ml of toluene, was added dropwise to a suspension of **7** (0.40 g, 0.52 mmol) in toluene. After 22 hr all of the complex had gone into solution and a white solid $(Ph_3PCH_2)^+(OSO_2F)^-$ was present. The light yellow green solution was filtered and toluene removed to give a pale yellow solid which was recrystallized from toluene and hexane. Authentic methyltriphenylphosphonium fluorosulfonate was prepared by mixing triphenylphosphine in benzene and adding it to a benzene solution of methyl fluorosulfonate. The filtered white solid gave an nmr spectrum which was identical with that obtained above.

J. The Interaction of Rhenium Pentacarbonyl Bromide with Methylene-triphenylphosphorane. $Re(CO)_5CH=Ph_3$. A solution of 0.54 g (1.97 mmol) of methylene-triphenylphosphorane in 15 ml of THF was added dropwise to a stirred solution of 0.4 g (0.985 mmol) of rhenium pentacarbonyl bromide in 35 ml of THF. A white solid formed immediately. After allowing the solution to stir for 4 hr, the solution was filtered from the white methyltriphenylphosphonium bromide $\delta_{CDCl_3}^{TMS}$ 3.2 ppm, $J_{PCH} = 13$ Hz, to give a bright yellow orange solution. Excess THF was removed to give an oily material which was recrystallized from THF–hexane, 0.25 g (41.3%), mp 100–110° dec.

Anal. Calcd for $C_{24}H_{16}O_5PRe$: C, 47.91; H, 2.68; O, 13.30; P, 5.15. Found: C, 48.11; H, 2.82; O, 13.03; P, 5.29.

These results were obtained from two different analysts and on two independently prepared samples.

K. The Interaction of Methylene-triphenylphosphorane with Iron Pentacarbonyl. $[Ph_3PCH_2]^+[Fe(CO)_5C(O)CHPh_3]^-$. Methylene-triphenylphosphorane (2.05 g, 7.4 mmol) in 20 ml of ether was slowly added to 0.73 g (3.72 mmol) of iron pentacarbonyl in 200 ml of ether which was cooled to 20°. A voluminous yellow precipitate formed immediately which was filtered from the reaction mixture, 2.78 g (97%), mp 130° dec. The yellow solid dissolves in THF to give a yellow slightly orange solution which is extremely sensitive to air. The same yellow adduct was obtained when methylene-triphenylphosphorane was added to a cold solution of iron pentacarbonyl in benzene, 2:1 molar ratio, respectively.

Anal. Calcd for $C_{43}H_{34}P_2O_5Fe$: C, 69.00; H, 4.58; P, 8.28; O, 10.69. Found: C, 69.22; H, 5.78; P, 8.18; O, 10.40.

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