Journal of Organometallic Chemistry, 61 (1973) 315–321

POSITIONAL ISOMERISM OF TRIPHENYLPHOSPHINE-NONACARBONYLMANGANESERHENIUM

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(Received March 22nd, 1973)

SUMMARY

The positional isomer *ax*-$(OC)_5MnRe(CO)_4PPh_3$ has been isolated and characterized by IR and ^{31}P NMR spectroscopy. Spectroscopic and kinetic evidence for the existence of the less stable isomer *ax*-$PPh_3(OC)_4MnRe(CO)_5$ in solution has also been obtained. The C–O stretching frequencies have been assigned on the basis of IR and Raman spectroscopic measurements.

INTRODUCTION

Mono- and bis-phosphine-substituted derivatives of $Mn_2(CO)_{10}$ have been well characterised[1-7]. The bis-phosphine derivatives of $Re_2(CO)_{10}$ are also well known[8-12] but only the monosubstituted compounds with L = $PMePh_2$ and PMe_2Ph have been isolated[11,12]. These derivatives are produced by substitution of the axial carbonyl groups except for the reactions of $Mn_2(CO)_{10}$ with pyridine or nitriles[2], and of $Re_2(CO)_{10}$ with PMe_2Ph[12], where the compounds *eq*-$M_2(CO)_9L$ have been isolated.

Phosphine substituted derivatives of the mixed metal carbonyl $MnRe(CO)_{10}$ have not previously been prepared. The compound $MnRe(CO)_9(PR_3)$ is of interest in that two isomers are possible, the phosphine being bonded either to the manganese or to the rhenium atom. Of particular interest is whether one or both isomers are formed as kinetic products of the reaction of $MnRe(CO)_{10}$ with PPh_3. We have isolated a complex of formula $MnRe(CO)_9PPh_3$ from this reaction and a comparison of its ^{31}P NMR spectrum with those of substituted derivatives of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ suggests that it is predominantly *ax*-$(OC)_5MnRe(CO)_4PPh_3$. Evidence for the presence of the other isomer in solution has also been obtained. The assignment of the vibrational spectra of the axial monosubstituted derivatives has been reconsidered on the basis of the IR and Raman spectra of the compound *ax*-$Re_2(CO)_9PPh_3$.

A similar example of a monosubstituted heteronuclear dimetal carbonyl, $MnCo(CO)_8PPh_3$, has been reported recently[13]. The IR spectrum showed the phosphine to be bonded to the cobalt atom and no evidence for the existence of the Mn–PPh_3 isomer was obtained.

EXPERIMENTAL

Materials

Dimanganese and dirhenium decacarbonyls (Strem Chemicals Inc.) were used as received. Triphenylphosphine (BDH Chemicals Ltd.) was recrystallized from ethanol and dried in vacuo for several days before use. Reagent grade solvents were used as received. Carbon monoxide was C.P. grade from The Matheson Co.

Preparation of Compounds

Compounds were prepared using standard vacuum line and Schlenk tube techniques. Precautions were taken to prevent exposure of the reaction mixtures to light.

Bis(triphenylphosphine)octacarbonyldimanganese. This complex was prepared by the method of Basolo and Wawersik[14]. The product was powdered, washed repeatedly with hexane and dried in vacuo before use. Recrystallization from dichloromethane–methanol was also found to be satisfactory. IR in cyclohexane: 1987w(sh) and 1963vs cm^{-1}. *Cf.* IR in *p*-xylene:[13] 1980w and 1959s cm^{-1}.

Mono(triphenylphosphine)nonacarbonyldimanganese was prepared according to the published procedure[3] but the recommended recrystallization from toluene–hexane was found to be unsuitable. Efficient separation of the desired product was achieved by chromatography on a foil-wrapped silica-gel (100–200 mesh) column made up in hexane. Unreacted $Mn_2(CO)_{10}$ was eluted with hexane, orange-red $Mn_2(CO)_9PPh_3$ with hexane–toluene (2/1 v/v), and orange $[Mn(CO)_4PPh_3]_2$ with toluene. After removal of solvent under reduced pressure, the product was washed with hexane and dried *in vacuo*. Yield: 40%. (Found*: C, 52.4; H, 2.54. $C_{27}H_{15}Mn_2O_9P$ calcd.: C, 52.1; H, 2.43%.)

Bis(triphenylphosphine)octacarbonyldirhenium. The published method for the preparation of this compound[10] gave very low yields but was effective when the reaction time was increased and a greater excess of ligand was used. Rhenium carbonyl (1.80 g, 2.76 mmol) and PPh_3 (2.16 g, 8.25 mmol) in xylene (80 ml) were refluxed for 20 h. The pale yellow solution was cooled and colourless crystals separated overnight. These were filtered off, washed with hexane (7 × 15 ml) and dried *in vacuo*. Yield: 2.30 g (75%). (Found: C, 47.6; H, 2.57. $C_{44}H_{30}O_8P_2Re_2$ calcd.: C, 47.1; H, 2.71%.) IR in dichloromethane: 2001vw, 1975w(sh) and 1960s cm^{-1} *Cf* IR in cyclohexane[9] 1988w and 1965vs cm^{-1}.

Mono(triphenylphosphine)nonacarbonyldirhenium. This new compound could not be prepared in a similar way to its dimanganese analogue since $[Re(CO)_4PPh_3]_2$ was the major product even with less than two equivalents of triphenylphosphine. Preparation was effected by reaction of $[Re(CO)_4PPh_3]_2$ with carbon monoxide, kinetic studies[15] having shown that this reaction proceeds to completion in hydrocarbon solvents at 125°C and complex concentrations below ca. 10^{-3} *M*. With larger concentrations the triphenylphosphine released during the reaction prevents it from going to completion, but separation of the mono- and bis-phosphine complexes by chromatography is efficient. A stream of CO was passed through a solution of

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* This microanalysis was by Alfred Bernhardt, Elbach über Engelskirchen, West Germany. All others were performed by A. B. Gygli, Microanalysis Laboratory, Toronto, Ontario.

$[Re(CO)_4PPh_3]_2$ (0.60 g, 0.54 mmol) in xylene (150 ml) at 130° for ca. 30 h, IR spectroscopy showing the reaction to have reached equilibrium. Solvent was removed under reduced pressure and $Re_2(CO)_9PPh_3$ was separated by chromatography from unreacted bis-phosphine complex and a small amount of decacarbonyl as described for the manganese analogue. Colourless crystals were isolated from the hexane–toluene eluate, washed with a little hexane, and dried in vacuo. Yield: 0.18 g (38%). (Found: C, 36.7; H, 1.84. $C_{27}H_{15}O_9PRe_2$ calcd.: C, 36.6; H, 1.71%.)

Bis(triphenylphosphine)octacarbonylmanganeserhenium. This new complex was prepared by a similar procedure to its dimanganese analogue[14]. Decacarbonylmanganeserhenium (0.70 g, 1.34 mmol), obtained by the reaction[16] of $Re(CO)_5Cl$ with $NaMn(CO)_5$ in freshly distilled anhydrous tetrahydrofuran, and PPh_3 (1.6 g, 6 mmol) were heated in xylene (50 ml) at 140° for 16 h. Yellow crystals of $MnRe(CO)_8(PPh_3)_2$ separated when the mixture was allowed to stand overnight at room temperature. The solvent was removed by decantation and the crystals were repeatedly washed with cold hexane. The product was recrystallized by addition of methanol to a dichloromethane solution. Yield: 0.81 g (61%). (Found: C, 53.5; H, 3.38. $C_{44}H_{30}MnO_8P_2Re$ calcd.: C, 53.4; H, 3.06%.) IR in dichloromethane: 1986w(sh), 1959s and 1909w cm^{-1}.

Mono(triphenylphosphine)nonacarbonylmanganeserhenium. This new complex was prepared by heating a solution of $MnRe(CO)_{10}$ (0.63 g, 1.2 mmol) and PPh_3 (0.28 g, 1.1 mmol) in xylene (10 ml) at 110° for ca. 50 h. Higher temperatures did not improve the yield and longer reaction times favoured the formation of the bis-phosphine complex. Chromatography of the product mixture on a silica-gel column as before, showed only one yellow band characteristic of the monophosphine complex. Elution with hexane–toluene led to isolation of yellow crystals of product. Yield: 0.55 g (60%). (Found: C, 43.0; H, 2.04. $C_{27}H_{15}MnO_9PRe$ calcd.: C, 42.9; H, 2.00%.)

Spectroscopic measurements

IR spectra in cyclohexane were measured in matched 1 mm path-length cells with sodium chloride windows with Perkin–Elmer 180 spectrophotometer. Spectra in toluene solutions required the use of 0.1 mm path length cells. The spectrophotometer was calibrated with polystyrene film, and the wavelengths given are believed to be accurate to ± 1 cm^{-1}. Routine spectra were run on a Perkin–Elmer 257 spectrophotometer.

Raman spectra were obtained for us by Mr. H. Huber with a Spex Laser Raman Spectrometer 1401, using a Carson Ar^+ laser excitation and calibrated with CCl_4.

The 24.28 MHz ^{31}P NMR spectra of concentrated toluene or chloroform solutions in 10 mm tubes were obtained for us by Professor M. C. Baird of Queen's University, Kingston, Ont., with a Bruker HX60 NMR spectrometer. The ^{31}P chemical shifts were measured relative to an external standard of 85% phosphoric acid with the machine locked on C_6F_6 contained in a 5 mm tube inside the sample tube. Some spectra were recorded by using the INDOR technique with the machine locked on tetramethylsilane.

RESULTS AND DISCUSSION

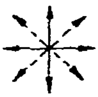
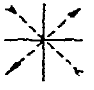
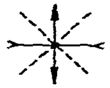
The ^{31}P NMR chemical shifts (in ppm) in chloroform solution were as follows:

PPh_3, +5.3; $[Mn(CO)_4PPh_3]_2$, −75.8 (br); $MnRe(CO)_8(PPh_3)_2$, −77.7 (br), −15.3; $[Re(CO)_4PPh_3]_2$, −17.5; $MnRe(CO)_9PPh_3$, −14.0; $Re_2(CO)_9PPh_3$, −14.9. The spectra of $[Mn(CO)_4PPh_3]_2$ and $MnRe(CO)_8(PPh_3)_2$ were obtained in $DCCl_3$ by use of the INDOR technique. The ^{31}P chemical shifts of PPh_3 and $Re_2(CO)_9PPh_3$ in toluene were +5.7 and −15.0 ppm, respectively. The solvent effects are quite small and the similarity of the chemical shifts in $Re_2(CO)_9PPh_3$, $MnRe(CO)_9PPh_3$ and $[Re(CO)_4PPh_3]_2$ shows that the isolated mono(triphenylphosphine)nonacarbonylmanganeserhenium is predominantly the Re–PPh_3 isomer $(OC)_5MnRe(CO)_4PPh_3$.

The coordination chemical shift, defined as $\delta_{\text{complex}}-\delta_{\text{ligand}}$, is negative (downfield) for PPh_3 attached to either manganese or rhenium but the shift is much greater for phosphorus attached to the former. This behaviour is the same as that observed in phosphine substituted complexes of the group (VI) carbonyls where, for all the phosphorus ligands, the coordination shift decreases on going down the group[17]. Thus, for $M(CO)_5PPh_3$ the chemical shifts are −55.3, −37.5 and −20.6 ppm

TABLE 1

IR AND RAMAN DATA IN C–O STRETCHING REGION FOR $M_2(CO)_9PPh_3$ COMPLEXES

	IR Frequency (cm^{-1}) (*Absorbances, relative to strongest band, given in parentheses*)				*Raman Frequency* (cm^{-1}) $Re_2(CO)_9PPh_3$		*Schematic representation of symmetry coordinates*[a]	
	$Mn_2(CO)_9$-PPh_3 *Cyclohexane*	$(OC)_5MnRe$-$(CO)_4PPh_3$ *Cyclohexane*	$Re_2(CO)_9PPh_3$ *Cyclohexane*	$Re_2(CO)_9PPh_3$ *Toluene*	*Toluene*	*Solid*		
ν_1	2091 (13)	2095 (18)	2107 (10)	2104 (19)	2104 vs (P)[b]	2102s		A_1 (R, IR)
ν_2	2010 (22)	2030 (28)	2034 (6)	2032 (11)	2032s (P)	2030m		A_1 (R, IR)
ν_4	—	—	—	—	2021s (DP)	2014s		B_1 (R)
ν_5	—	1973w(sh)	1976w(sh)	—	1969w(sh)	1965w(sh)		B_2 (R)
ν_6	1995 (100)	1988 (100)	1998 (100)	1991 (100)	1987s (DP)	1984m		E (R, IR)
ν_7	1973 (17)	1969 (35)	1968 (25)	1960 (15)	1961m (DP)	1956m		E (R, IR)
ν_3	1938 (18)	1946 (18)	1941 (24)	1934 (19)	1929w (P)	1939w		A_1 (R, IR)

[a] Viewed along M–M bond axis with PPh_3 above plane of paper. [b] P, polarized: DP, depolarized.

for M = Cr, Mo and W, respectively, and presumably the same factors[17,18] govern the trends in both series.

The NMR signal for phosphorus attached to manganese is broad, whereas that for phosphorus attached to rhenium is quite sharp. Both manganese and rhenium have nuclear quadrupole moments [$Q(^{55}Mn)$, 0.6; $Q(^{185}Re)$, 2.8 and $Q(^{187}Re)$ 2.6, all in units of $e \times 10^{24}$ cm^2][19] which will tend to destroy the spin–spin coupling by increasing the relaxation rates of the metal nuclei[20]. The greater quadrupole moments of the rhenium nuclei are probably one factor contributing to the sharper resonance of the rhenium-bonded phosphorus but the electric field gradients at the nuclei and the magnitude of the metal–phosphorus coupling constants are other factors involved[21].

The carbonyl stretching frequencies for the three monophosphine derivatives, including Raman data for $Re_2(CO)_9PPh_3$, are listed in Table 1. If the molecules belong to the point group C_{4v}, as expected (*e.g.* ref. 2), they should possess seven fundamental C–O stretching modes all of which are Raman active and five of which are also IR active. The Raman spectrum of $Re_2(CO)_9PPh_3$ shows the expected seven bands and the polarization measurements enable the three totally symmetric A_1 modes to be assigned. One of the bands in the Raman spectrum is clearly absent in the IR and is assigned to one of the two B modes. Of the remaining three bands, one coincides with the strongest band in the IR and is clearly the E mode as shown. The other band of medium intensity in both the IR and Raman spectra is assignable to the other E mode, leaving the remaining band to be designated as the second B mode. Corresponding bands in the IR spectra of the other monophosphines are similarly assigned.

The frequencies of the three A_1 modes are assigned to particular normal modes as shown in Table 1 on the basis of the low frequency expected for the vibration of the axial carbonyl ligand[2], and the high Raman intensity expected for the highest frequency ν_1 vibration. The ν_1 and ν_2 A_1 modes derive their intensity in the IR from transition dipole moments along the z (M–M bond) axis. This is mainly possible for the ν_1 mode because of the asymmetry introduced by the phosphine ligand. The intensity of the ν_1 A_1 mode, relative to the corresponding ν_2 A_1 mode, varies with L in $Mn_2(CO)_9L$ as follows: L = PF_3, 0.05; $P(OPh)_3$, 0.3; PPh_3, 0.6; $P(n\text{-}Bu)_3$, 0.3. When L = PPh_3 the relative intensities are $Mn_2(CO)_9PPh_3$, 0.6; $(OC)_5MnRe(CO)_4PPh_3$, 0.5; $(PPh_3)(OC)_4MnRe(CO)_5$, ca. 2 (see below); $Re_2(CO)_9PPh_3$, 1.7. It is significant that the lowest intensity ratio is that shown by $Mn_2(CO)_9PF_3$ in which the phosphine is closest in nature to carbon monoxide and would therefore be expected to introduce the least electronic asymmetry. The relatively large value for L = PPh_3 in $Mn_2(CO)_9L$ might be due to steric effects. Indeed, the ratios of the intensities correlate very well with the respective ligand cone angles[22]. The relative intensities are clearly more affected by changing the metal atoms rather than the phosphine ligand and it would appear that such data might provide additional insight into the nature of the metal–metal bonds in these complexes.

The two B modes are individually assigned on the basis that the vibrating carbonyls attached to the metal with the phosphine ligand will have a lower frequency. In addition, the fact that this band (ν_5) has some intensity in the IR is explained by the lowering of the local symmetry induced by the triphenylphosphine ligand.

These assignments support those made for $Mn_2(CO)_9PPh_3$ from IR data alone[2] with the exception of those of the two bands of lowest frequency. Our Raman data show that the lowest frequency band in $Re_2(CO)_9PPh_3$ is due to the A_1 mode of

TABLE 2

IR SPECTRA OF POSITIONAL ISOMERS OF *ax*-$MnRe(CO)_9PPh_3$
(produced *in situ* in decalin by treating of $MnRe(CO)_8(PPh_3)_2$ with carbon monoxide at 120°C).

	$A_1(\nu_1)$	$A_1(\nu_2)$	$E(\nu_6)$	$E(\nu_7)$	$A_1(\nu_3)$
$(OC)_5MnRe(CO)_4PPh_3$	2095 (8)	2030 (15)	1990 (100)[a]	1971 (18)	1949 (9)
$PPh_3(OC)_4MnRe(CO)_5$	2108 (8)	2046 (ca. 4)	2005 (100)[a]	—	1929 (20)
$MnRe(CO)_{10}$[b]	2124vw	2054m	2017s	—	1978m

[a] Ratio of absorbance of Re–PPh_3 and Mn–PPh_3 is ca. 3:1; [b] Ref. 16.

the axial carbonyl rather than to the less intense of the two *E* modes. It seems very likely, therefore, that this is also the case in $Mn_2(CO)_9PPh_3$ and that the assignments of the two low frequency bands made by Ziegler *et al.*[2] should be reversed.

The monophosphine complex produced initially during the reaction of $MnRe(CO)_{10}$ with PPh_3 in decalin shows in the IR only the five bands characteristic of the Re–PPh_3 isomer. Reaction in decalin, at 90–120°, of $MnRe(CO)_8(PPh_3)_2$ under 1 atm of carbon monoxide reveals evidence for the existence of the Mn–PPh_3 isomer. The IR bands of the product solution when all the bisphospine complex has reacted are listed in Table 2. For product solutions from a number of runs, the bands at 2108 and 1929 cm^{-1} show a very constant intensity ratio to the strong band at 2005 cm^{-1} although the weak band at 2046 cm^{-1} varies somewhat in relative intensity. Compared with $MnRe(CO)_{10}$, the axial triphenylphosphine ligand attached to the rhenium decreases the observed radial carbonyl stretching frequencies by a little more than twice as much as one attached to the manganese atom. The missing *E* mode in $(PPh_3)(OC)_4MnRe(CO)_5$ might be concealed as a weak shoulder to the 1971 cm^{-1} band in the former isomer. The vibrational frequencies of the axial carbonyl ligand also follow a regular pattern in that replacement of $(PPh_3)(OC)_4Mn$, attached to $M(CO)_5$, by $(PPh_3)(OC)_4Re$ increases the frequency by 8 and 12 cm^{-1} when M = Mn and Re, respectively. The IR spectra of these solutions are quite consistent with the presence of $(PPh_3)(OC)_4MnRe(CO)_5$ together with the isolated and characterized Re–PPh_3 isomer.

Further evidence that the new bands are indeed due to the Mn–PPh_3 isomer is provided by the following results. Reaction of the mixture under carbon monoxide at 150° leads to the formation of $MnRe(CO)_{10}$, the IR bands attributed to the Mn–PPh_3 isomer decreasing with a first order rate constant of 1.1×10^{-3} s^{-1} and those from the Re–PPh_3 isomer decreasing with a rate constant of 2.4×10^{-4} s^{-1}. Reaction with an excess of triphenylphosphine under nitrogen leads to reformation of $MnRe(CO)_8(PPh_3)_2$, the Mn–PPh_3 and Re–PPh_3 isomers reacting with rate constants of 3.7×10^{-3} s^{-1} and 7×10^{-4} s^{-1}, respectively. This is fully consistent with the existence in solution of a kinetically less stable Mn–PPh_3 isomer. If it is assumed that the ν_6 *E* modes of both isomers have the same absolute intensities, then the ratio of the Re–PPh_3 and Mn–PPh_3 isomers produced from $MnRe(CO)_8(PPh_3)_2$ under these conditions is ca. 3/1, this product ratio probably being kinetically, rather than thermodynamically, controlled.

The kinetic behaviour observed is unexpected. At 130° PPh_3 is displaced about 3×10^4 times more rapidly by carbon monoxide from $[Mn(CO)_4PPh_3]_2$[23]

than from $[Re(CO)_4PPh_3]_2$[15] whereas carbon monoxide is only about 80 times more rapidly displaced from $Mn_2(CO)_{10}$ than from $Re_2(CO)_{10}$ at this temperature[24]. Reaction of $MnRe(CO)_8(PPh_3)_2$ with carbon monoxide would be expected to give the Re–PPh_3 isomer as the main kinetic product, and reaction of $MnRe(CO)_{10}$ with triphenylphosphine would be expected to give mainly the Mn–PPh_3 product. Clearly the asymmetry of the metal–metal bond has a profound effect on the course of these reactions.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the National Research Council of Canada and from Erindale College, and useful discussions with Professors G. A. Ozin and M. Baird.

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