The Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. Part 1. Homogeneous Catalysis of Organic Reactions by Bromo(carbonyl)-hydridotris(triphenylphosphine)osmium(II)†

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The title compound catalyses C=C bond migration, isomerisation of allyl alcohol, hydrogenation of ayclic and cyclic olefins, dienes, acetylenes, aldehydes, ketones, α,β-unsaturated aldehydes and ketones, and hydroformylation of alkenes under moderate reaction conditions. High selectivities have been observed in the hydrogenation of conjugated and unconjugated dienes to monoenes, C≡C to C=C bonds, α,β-unsaturated aldehydes to unsaturated alcohols, and α,β-unsaturated ketones to saturated ketones; L-carvone [2-methyl-5-(1-methylethenyl)cyclohex-2-en-1-one] may be selectively reduced to 2-methyl-5-(1-methylethyl)cyclohex-2-en-1-one or 2-methyl-5-(1-methylethyl)-cyclohexanone depending on the reaction conditions.

Homogeneous catalysis by use of third-row transition-metal complexes, and particularly those of osmium, remains a largely unexplored field. The fact that 5*d* metals form stronger bonds than their 3*d* and 4*d* congeners with hydride, olefin, alkyl, phosphine, and other ligands typically involved in catalytic transformations,[1] has led to the general assumption that reactions conforming catalytic cycles, such as Lewis base addition–elimination, insertion–deinsertion, *etc.*, are too slow for third-row metal complexes to be of any practical use in catalysis. On the other hand, a number of osmium compounds have been synthesised and characterised to serve as stable models of intermediates proposed to intervene in catalytic reactions involving the generally more reactive 4*d* metals.[2]

Consequently, the catalytic potential of osmium complexes has been hitherto essentially neglected. The trinuclear cluster $[Os_3(CO)_{12}]$ is an active catalyst for alkene isomerisation,[3] alkyne cyclotrimerisation,[4] C–N bond activation,[5] hydroformylation,[6] water–gas shift,[6,7] and CO hydrogenation[8] reactions in solution. The dihydrido-derivative $[Os_3H_2(CO)_{10}]$ has been reported to hydrogenate olefins in solution[9] and when supported on silica.[10] We have recently discovered that a number of other tri- and tetra-nuclear osmium clusters can serve as efficient catalysts for C=C bond hydrogenation under moderate reaction conditions.[11]

For mononuclear complexes, however, examples of active catalysts are very scarce. Vaska[12] and Mitchell[13] have mentioned the ability of $[OsH(Cl)(CO)(PPh_3)_3]$ to hydrogenate C=C bonds; Chatt and co-workers[14] briefly described the isomerisation and hydrogenation of octenes catalysed by $[OsH_2(PEtPh_2)_4]$, $[OsH_2(CO)(PEtPh_2)_3]$, and $[OsH_4(PEtPh_2)_3]$. Olefin hydrogenation by use of $[OsH(Cl)(CO)(PPh_3)_3]$, $[OsH_3(PPh_3)_3]$, and $[OsH(Cl)_2(AsPh_3)_3]$,[15] as well as hydroformylation catalysed by an unspecified osmium salt complexed by phosphine ligands[16] have been claimed in the patent literature.

In this paper we report the catalytic properties of a well defined, stable, mononuclear osmium(II) complex, *viz.* $[OsH(Br)(CO)(PPh_3)_3]$, in a variety of organic reactions in solution. The versatile reactivity of this compound, together with its selectivity properties show that homogeneous catalysis by osmium complexes may be a more promising field than previously realised. A preliminary account of this work has already appeared.[17]

Results and Discussion

From our previous work on the catalytic properties of ruthenium complexes[18] it seemed probable that analogous osmium compounds could also be of use as catalysts for homogeneous organic reactions. We therefore investigated the catalytic behaviour of the complex $[OsH(Br)(CO)(PPh_3)_3]$ (**1**), which is easily prepared and thermally and oxidatively stable.[19,20]

Isomerisation and Hydrogenation Reactions.—Hex-1-ene is rapidly isomerised by a toluene solution of (**1**) under N_2 to a mixture of *cis*- and *trans*-hex-2-ene [Figure 1(*a*)]; no double bond migration to the 3-position was observed even after 24 h reaction. Under dihydrogen at atmospheric pressure both hex-1-ene and *trans*-hex-2-ene are isomerised to the same equilibrium mixture; hydrogenation to the alkane takes place simultaneously, albeit at a much slower rate. At longer reaction times, n-hexane becomes the major product [Figure 1(*b*) and (*c*)].

Cyclohexa-1,3-diene is also isomerised by a toluene solution of (**1**) to the deconjugated product cyclohexa-1,4-diene, at a slower rate than that observed for hex-1-ene [Figure 2(*a*)]. Under 1 atm H_2 selective hydrogenation *to the mono-olefin* is observed, together with the faster isomerisation reaction [Figure 2(*b*)]; cyclohexene is hydrogenated very slowly under these conditions [Figure 2(*c*)] but rapid reduction to the alkane can be achieved by raising the hydrogen pressure to 5 atm.

A number of monohydride catalysts for the reduction of dienes to monoenes have been described,[21a] but this is, to our knowledge, the first example of an active and selective osmium system; furthermore, our results show that unlike the well known $[CoH(CN)_5]^{3-}$ catalyst,[21a,22] which only reduces conjugated dienes to monoenes, (**1**) is capable of effecting the selective hydrogenation of conjugated *as well* as unconjugated dienes.

The C≡C bond in phenylacetylene can also be selectively

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† *Non-S.I. unit employed:* atm = 101 325 Pa.

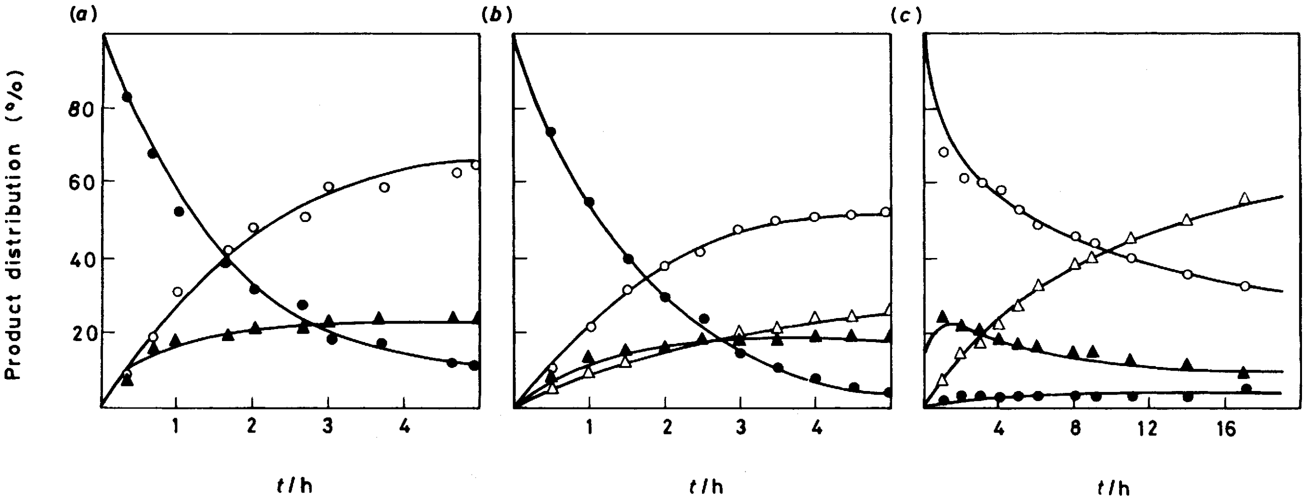


Figure 1. Isomerisation and hydrogenation of hex-1-ene by [OsH(Br)(CO)(PPh$_3$)$_3$]: 100 °C, [substrate]:[catalyst] = 100:1, in toluene; ● hex-1-ene, ○ *trans*-hex-2-ene, ▲ *cis*-hex-2-ene, △ n-hexane; (*a*) 1 atm N_2; (*b*), (*c*) 1 atm H_2

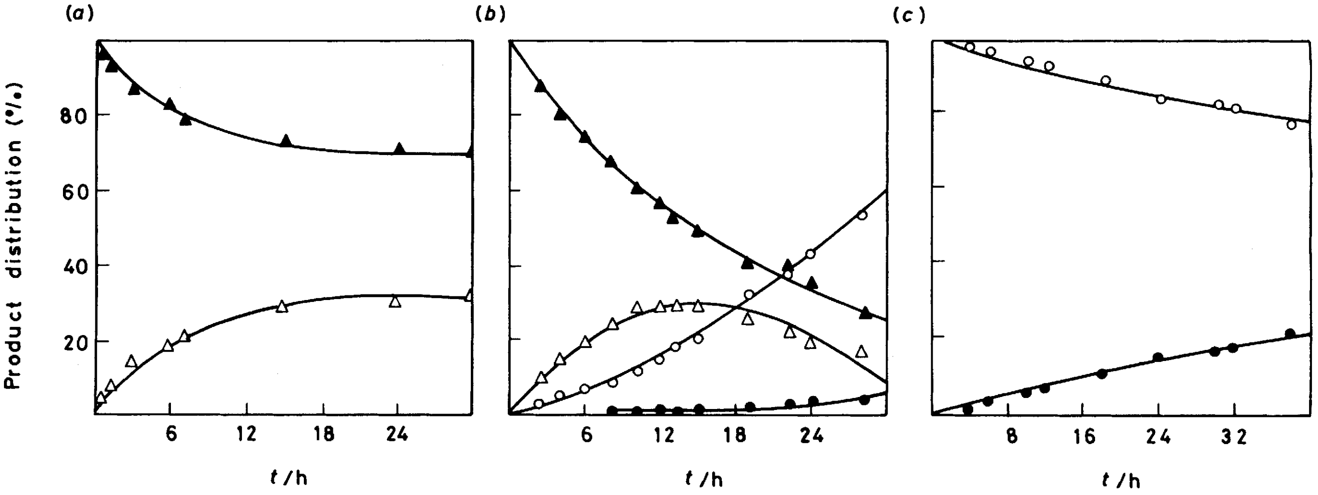


Figure 2. Isomerisation and hydrogenation of cyclohexa-1,3-diene and hydrogenation of cyclohexene by [OsH(Br)(CO)(PPh$_3$)$_3$]: conditions as in Figure 1; ▲ cyclohexa-1,3-diene, △ cyclohexa-1,4-diene, ○ cyclohexene, ● cyclohexane; (*a*) 1 atm N_2; (*b*), (*c*) 1 atm H_2

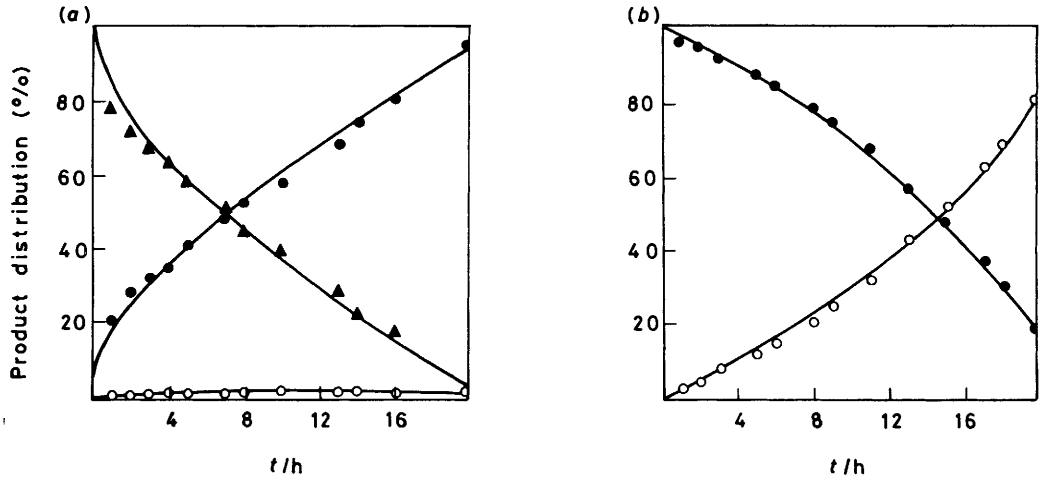


Figure 3. Hydrogenation of (*a*) phenylacetylene and (*b*) styrene by [OsH(Br)(CO)(PPh$_3$)$_3$]: conditions as in Figure 1; H_2 at atmospheric pressure; ▲ phenylacetylene, ● styrene, ○ ethylbenzene

Table 1. Homogeneous hydrogenation by $[OsH(Br)(CO)(PPh_3)_3]$[a] (all reactions in toluene)

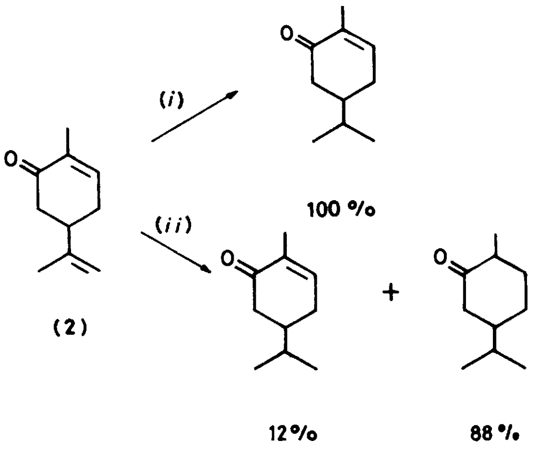
Reactants	T/°C	P/atm	t/h	Turnover number	Product distribution (%)	
Propionaldehyde[b]	150	30	1.7	100	Propan-1-ol	(100)
Benzaldehyde	100	1	24	85	Benzyl alcohol	(100)
Acetone	150	68	3	15	Propan-2-ol	(100)
Crotonaldehyde	150	5	0.8	35	But-2-en-1-ol	(15)
					Butyraldehyde	(20)
					Butan-1-ol	(65)
Crotonaldehyde	100	1	0.8	10	But-2-en-1-ol	(50)
					Butyraldehyde	(50)
Cyclohex-2-en-1-one	100	1	24	80	Cyclohexanone	(100)
Cyclohex-2-en-1-one	150	5	2	100	Cyclohexanone	(69)
					Cyclohexanol	(31)
Cyclohex-2-en-1-one + propan-2-ol[c]	100		7	90	Cyclohexanone	(89)
					Cyclohexanol	(11)

[a] [Substrate]:[catalyst] = 100:1, unless stated otherwise. [b] [Substrate]:[catalyst] = 1 000:1. [c] [Propan-2-ol]:[substrate] = 15:1, under N_2.

Table 2. Product distribution in the homogeneous hydroformylation of hex-1-ene by $[OsH(Br)(CO)(PPh_3)_3]$[a]

CO:H_2	Turnover number	n-Hexane (%)	*trans*-Hex-2-ene (%)	*cis*-Hex-2-ene (%)	Heptanal (%)	2-Methylhexanal (%)	C_7 Alcohols (%)
1:1	30	13	17	7	40	17	6
2:1	76	5	16	7	45	22	5
3:1	24	8	14	8	46	16	8

[a] In toluene; [substrate]:[catalyst] = 100:1, 150 °C, 100 atm, 24 h.



Scheme. Hydrogenation of L-carvone by $[OsH(Br)(CO)(PPh_3)_3]$: (*i*) 1 atm H_2, (*ii*) 5 atm H_2; 100 °C, in toluene

reduced by (1) under H_2 at atmospheric pressure; after *ca.* 100 catalytic cycles the selectivity for the production of styrene is close to 100% [Figure 3(*a*)]. In the absence of the alkyne, styrene is reduced to ethylbenzene at a comparable rate [Figure 3(*b*)], but the presence of as low as 1% phenylacetylene suppresses the reduction of the double bond almost completely.

Examples of selective reduction of alkynes to alkenes are still uncommon; complete hydrogenation, as well as oligomerisation and polymerisation of alkynic substrates is often observed in the presence of transition metals.[21b] We believe this to be the first report of a fairly active and highly selective osmium catalyst for the reduction of C≡C to C=C bonds.

Other hydrogenation reactions catalysed by (1) are reported in Table 1. Aldehydes and ketones are efficiently reduced to their corresponding alcohols as the sole products under moderate reaction conditions. There are no prior examples in the literature for the osmium-catalysed homogeneous hydrogenation of carbonyl groups. Crotonaldehyde is hydrogenated to the saturated aldehyde, the unsaturated alcohol, or the fully reduced product, depending on the reaction conditions. At 100 °C and 1 atm H_2, a 1:1 mixture of but-2-en-1-ol and butyraldehyde is produced, whilst no butan-1-ol is observed (Table 1). This type of selectivity for C=O *versus* C=C bond reduction is higher than that observed for analogous ruthenium catalysts.[23]

Cyclohex-2-en-1-one, on the other hand, is exclusively reduced to cyclohexanone under H_2 at atmospheric pressure, or more rapidly, in boiling propan-2-ol under N_2; a small amount of cyclohexanol is detected in the latter case. Interestingly, hydrogenation of cyclohex-2-en-1-one is faster than that of cyclohexene, indicating that the presence of the carbonyl group has a favourable effect on the reduction of the C=C bond; this could be attributed to either an enhanced co-ordination strength of the substrate to the metal, or to the carbonyl making the double bond more susceptible to nucleophilic attack.

Allyl alcohol is isomerised to propionaldehyde by (1) in toluene at 100 °C under N_2. When a 1:1 mixture of substrate and product is formed (*i.e.*, 50% conversion) the reaction stops. Although some formation of the corresponding hemiacetal can be detected by i.r. spectroscopy, this side reaction alone cannot explain our observation, since the catalytic solution remains inactive after further addition of allyl alcohol; it is possible that the catalyst deactivation is due to a strong interaction between the complex and the aldehyde, which impedes co-ordination of the substrate to the metal centre.

As a further test of the reactivity of (1) we have studied the hydrogenation of L-carvone (2) [2-methyl-5-(1-methylethenyl)-cyclohex-2-en-1-one], a model compound containing exocyclic and endocyclic C=C bonds, as well as a carbonyl group. As shown in the Scheme, the exocyclic C=C bond is specifically reduced at 100 °C and atmospheric pressure (30 turnovers in 24 h); the rate of the reaction is increased (2—3 fold) by the presence of air without affecting the selectivity, but the solution develops a dark brown colour and the catalyst is transformed into an uncharacterised mixture. Raising the hydrogen pressure to 5 atm results in the reduction of both C=C bonds (65 turnovers in 5 h), whilst no carvomenthol [2-methyl-5-(1-methylethyl)cyclohexanol], the fully hydrogenated product, could be detected by g.l.c. or ^{13}C n.m.r. The specific hydrogenation of the isopropylidene group in carvone has been previously reported using Wilkinson's catalyst.[24]

Hydroformylation of Hex-1-*ene*.—Although hydroformylation of alkenes catalysed by Co, Rh, and Ru complexes has been extensively studied,[25] the use of osmium compounds in this reaction has been limited to $[Os_3(CO)_{12}]$,[6] and an unspecified osmium salt complexed by phosphine ligands mentioned in a patent.[16] Complex (**1**) catalyses the hydroformylation of hex-1-ene in toluene under moderate reaction conditions. As shown in Table 2, both the rate and the product distribution are dependent on the gas-phase composition. The highest activity and selectivity are achieved at a $CO:H_2$ ratio of 2:1, corresponding to a 76% conversion (67% aldehydes) and an *n*/*i* (normal/iso aldehyde) ratio of *ca*. 2. Further increases in the proportion of CO result in a marked drop in the rate of the reaction, and little effect on the product distribution.

Complex (**1**) is quantitatively transformed during the reaction into $[OsH_2(CO)_2(PPh_3)_2]$ (identified by its i.r. spectrum) and thus, the active species must be a closely related compound, probably the 16-electron complex $[OsH_2(CO)_2(PPh_3)]$. This behaviour is similar to that observed in the Ru^{II}-catalysed hydroformylation of alkenes.[26] In contrast, complex (**1**) is recovered unchanged from most of the isomerisation and low-pressure hydrogenation reactions described above.

Conclusions

The complex $[OsH(Br)(CO)(PPh_3)_3]$ is a very efficient catalyst for a variety of synthetically useful organic reactions in solution, since it combines high activity and selectivity under mild reaction conditions with ease of preparation, handling, and recycling.

This illustrates the fact that osmium complexes may be more active and versatile in homogeneous catalysis than is generally realised, provided that the ligands and the reaction conditions are chosen appropriately. This opens a rather promising and largely unexplored area of research; in following papers of this series we will provide further examples of catalytically-active mononuclear osmium complexes.

Experimental

Materials.—Solvents (Fischer) were freshly distilled from appropriate drying agents under nitrogen. Olefins (Aldrich) were passed through a column of activated γ-alumina and distilled from sodium wire under nitrogen immediately before use. Other organic reagents (Aldrich) were distilled and dried over molecular sieves. $[OsH(Br)(CO)(PPh_3)_3]$ was prepared according to known procedures,[19] or purchased from Strem Chemicals Inc. and used as received.

Catalytic Runs.—*Low-pressure hydrogenation reactions*. In a three-necked flask (100 cm^3) equipped with a stirring bar, a reflux condenser thermostatted to 0 °C, a gas bubbler, and a stopcock stoppered with a rubber septum, was introduced a deoxygenated toluene solution (3.0×10^{-6} mol dm^{-3}) of $[OsH(Br)(CO)(PPh_3)_3]$. The deoxygenated substrate (3.0×10^{-4} mol dm^{-3}) was added through the septum and the mixture flushed with hydrogen at room temperature. The flask was then introduced into a silicone oil-bath at the desired temperature, and stirring initiated; this is taken as the zero time for the reaction. A constant bubbling (*ca*. 1 bubble s^{-1}) of hydrogen was maintained during the course of the reaction. Sampling was carried out periodically by opening the stopcock and syringing *ca*. 0.2 cm^3 of the solution through the septum.

For the hydrogen-transfer reactions, toluene was replaced by propan-2-ol and the mixture was maintained under vigorous reflux under nitrogen. Isomerisation reactions were carried out in closed Schlenk tubes under nitrogen.

High-pressure reactions. The catalyst, substrate, solvent (concentrations as above), and a stirring bar were introduced into a glass-lined stainless steel autoclave (125 cm^3, Parr Instruments), which was purged three times with the appropriate reaction gas at room temperature and then charged to the desired pressure. The autoclave was introduced into a silicone oil-bath at the reaction temperature, and stirring started immediately.

Hydrogenation reactions were carried out at constant pressure by continuous hydrogen feeding from a high-pressure reservoir; in the hydroformylation experiments, the autoclave was charged and isolated, and the pressure was allowed to drop during the run. At the desired time, the autoclave was introduced into ice to quench the reaction, the excess pressure was released and the products immediately analysed.

Product Analysis.—Products were analysed by g.l.c. using Varian 3700 instruments with flame ionisation or thermal conductivity detectors, coupled with Varian CDS-111 or CDS-401 (Vista) data systems. Stainless steel columns (3 m) were used as follows: 10% SP-2100 on Supelcoport for isomerisation of cyclohexa-1,3-diene, allyl alcohol, and hydrogenation of cyclohexene and benzaldehyde; 10% SE-30 on chromosorb for isomerisation of hex-1-ene; 16% bis(2-methoxyethyl) adipate on chromosorb for hydrogenation of hex-1-ene and *trans*-hex-2-ene; 10% 1,2,3-tris(2-cyanoethoxy)propane on Supelcoport for hydrogenation of cyclohexa-1,3-diene, phenylacetylene, and styrene; 10% Carbowax on chromosorb for hydrogenation of cyclohex-2-en-1-one, 10% SP-2330 on Supelcoport for hydrogenation of crotonaldehyde; a system of two columns in series [16% bis(2-methoxyethyl) adipate and Carbowax on chromosorb] was used to analyse hydroformylation mixtures.

Hydrogenation products of L-carvone were analysed by a combination of g.l.c. (3% SP 2300 on Supelcoport column) and ^{13}C n.m.r. Spectra were recorded at 25.14 MHz using a Varian XL-100 instrument adapted for Fourier-transform by Nicolet. Data acquisition and analysis was performed with the NIC 1180 computer on line with the spectrometer. Resonances corresponding to the hydrogenation products were assigned by comparison with the spectrum of pure L-carvone (type of carbon and line intensity). All peaks were assigned by attached proton test experiments,[27] with the exception of two close impurity resonances around 134 p.p.m. (from $SiMe_4$). Relative concentrations were obtained using peak areas calculated from line fitting of each resonance in a gate decoupled spectrum with a long (120 s) equilibration delay.

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References

1 J. P. Collman and L. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Menlo Park, California, 1980, p. 49.
2 R. D. Adams and J. P. Selegue, in 'Comprehensive Organometallic

Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, ch. 33.

3 R. P. Ferrari and G. A. Vaglio, *Inorg. Chim. Acta*, 1976, **20**, 141.

4 G. A. Vaglio, O. Gambino, R. P. Ferrari, and G. Cetini, *Inorg. Chim. Acta*, 1973, **7**, 193.

5 Y. Shvo and R. M. Laine, *J. Chem. Soc., Chem. Commun.*, 1980, 753.

6 H. C. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann, and R. Pettit, *J. Am. Chem. Soc.*, 1977, **99**, 8323.

7 A. D. King, R. B. King, and D. B. Yang, *J. Chem. Soc., Chem. Commun.*, 1980, 529.

8 M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1976, **98**, 1296; R. J. Daroda, J. R. Blackborow, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1980, 1098, 1101.

9 J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.*, 1976, **98**, 1956.

10 B. Besson, A. Choplin, L. D'Ornelas, and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 1982, 843.

11 R. A. Sánchez-Delgado, J. Puga, and M. Rosales, *J. Mol. Catal.*, 1984, **24**, 221.

12 L. Vaska, *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 89.

13 T. R. B. Mitchell, *J. Chem. Soc. B*, 1970, 823.

14 B. Bell, J. Chatt, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1973, 997.

15 P. Fotis and J. D. McCollum, U.S.P. 3 324 018/1967.

16 L. Slaugh and R. D. Millineaux, U.S.P. 3 239 571/1966.

17 R. A. Sánchez-Delgado, A. Andriollo, and N. Valencia, *J. Chem. Soc., Chem. Commun.*, 1983, 44.

18 R. A. Sánchez-Delgado and O. L. de Ochoa, *J. Organomet. Chem.*, 1980, **202**, 427; R. A. Sánchez-Delgado, A. Andriollo, O. L. de Ochoa, T. Suárez, and N. Valencia, *ibid.*, 1981, **209**, 77; R. A. Sánchez-Delgado, A. Andriollo, K. Doppert, C. Ramírez, and N. Valencia, *Acta Cient. Venez.*, 1982, **33**, 23.

19 L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, 1961, 1262.

20 P. L. Orioli and L. Vaska, *Proc. Chem. Soc. London*, 1962, 333.

21 (*a*) B. R. James, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 8, p. 311; (*b*) *ibid.*, pp. 347—350.

22 B. R. James, 'Homogeneous Hydrogenation,' Wiley Interscience, New York, 1973, ch. 10.

23 R. A. Sánchez-Delgado, A. Andriollo, and N. Valencia, *J. Mol. Catal.*, 1984, **24**, 217.

24 A. J. Birch and K. A. M. Walker, *J. Chem. Soc. C*, 1966, 1894.

25 R. L. Pruett, *Adv. Organomet. Chem.*, 1979, **17**, 1.

26 R. A. Sánchez-Delgado, J. S. Bradley, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 399.

27 S. L. Patt and J. N. Shoolery, *J. Magn. Reson.*, 1982, **46**, 535.

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