AN ESR STUDY OF LIGAND EXCHANGE IN ORGANOMETALLIC RADICAL COMPLEXES. SUBSTITUTION OF GROUP VA ORGANOMETALS IN THE QUINONE–RHENIUM CARBONYL PARAMAGNETIC COMPLEXES

K.A.M. CREBER and J.K.S. WAN

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Stable heterobinuclear and trinuclear metal organic radical complexes containing rhenium carbonyl and group VA organometals are prepared by ligand exchange reactions. ESR observations provide further insights into the dynamics and the possible exchange sites.

The roles of paramagnetic intermediates in organometallic and catalytic processes have been receiving increased attention in recent years. Because of the wide potential applications of ESR spectroscopy and the CIDEP [1] technique to free radical reactions, we have currently initiated a series of systematic investigations aiming at some controversial organometal paramagnetic intermediates which have to date escaped ESR detection. Among such challenges are the possible substituted rhenium carbonyl radicals such as $Re(CO)_4PPh_3^{\cdot}$ and $Re(CO)_3(PR_3)_2^{\cdot}$ which have been proposed, based upon chemical evidence, as the radical intermediates in the reaction of $(CO)_5ReRe(CO)_5$ with organophosphorus compounds [2].

It has been well established that lability of the CO ligands is a characteristic of the 17-electron metal carbonyl species [3] and ESR evidence has been obtained for the formation of moderately stable organophosphorus-substituted manganese carbonyl radicals in solution by photosubstitution reactions [4,5]. Other methods including the usual nitroxide spin trapping technique have also provided evidence for some binuclear transition metal carbonyl radicals in solution [6].
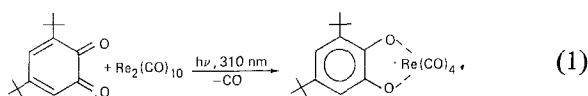
In most cases it was not possible to isolate the radical species for a full spectroscopic characterization. As an extension of our recent work using ortho-quinones and dicarbonyl compounds to "trap" reactive metal centered radicals [7,8], we have succeeded in developing a powerful combined technique of ESR/HPLC (high-performance liquid chromatography) to isolate some of the stable quinone–rhenium carbonyl radical complexes for a full spectroscopic characterization, including UV/visible absorption and emission as well as IR spectroscopy [9]. In this report we present another new aspect of the "spin trapping" chemistry to study the ESR of the controversial binuclear group VA organometal-substituted rhenium carbonyl radicals. We began by preparing the stable quinone–rhenium carbonyl radical complex [9] in solution and further allowed the radical to exchange its "labile" carbonyl ligands with group VA organometals.

Electron spin resonance measurements were recorded on a Bruker 420 X-band spectrometer with 100 kHz field modulation. The temperature was varied by flowing thermostatted nitrogen past the sample. To enhance spectral resolution, second-derivative mode of presentation was obtained in the usual way with the first phase-sensitive detector operating at 100 kHz and a second one operating at 50 kHz. *g* factors were measured using a Bruker NMR oscillator to monitor the field and a Hewlett–Packard 5342 frequency counter to measure the microwave frequency. Decacarbonyldirhenium was supplied by Strem Chemicals and 3,5-di-*t*-butyl-*o*-benzoquinone was obtained from Aldrich. Various group VA organo-

metal ligands were gifts from Mr. Richard Smith and Professor M.C. Baird.

The persistent radical complex of rhenium carbonyl with 3,5-di-*t*-butyl-*o*-benzoquinone (DTBQ) was prepared in benzene [9] by irradiating the green solution containing $Re_2(CO)_{10}$ and DTBQ with a 200 W mercury super-pressure lamp equipped with a monochromator set at 310 nm under nitrogen atmosphere. The color of the solution was changed to red due to the formation of the DTBQ$\overset{.}{-}$Re$(CO)_4$ radical complex:

$$\text{(structure)} + Re_2(CO)_{10} \xrightarrow[-CO]{h\nu, 310 \text{ nm}} \text{(structure)} \cdot Re(CO)_4 \cdot \qquad (1)$$

In the presence of an "excess" quinone, both HPLC and spectrophotometric monitoring of $Re_2(CO)_{10}$ indicate that more than 90% of the rhenium carbonyls is converted to the radical complex. A similar experiment using organophosphine instead of DTBQ did not yield any observable radical complex. However, when organophosphine was added to a red benzene solution containing the DTBQ$\overset{.}{-}$Re$(CO)_4$ radical complex, the color of the solution immediately changed to dark blue and the ESR observation showed the formation of a "new" species with different spectral parameters. Fig. 1 shows the ESR spectra of the DTBQ$\overset{.}{-}$Re$(CO)_4$ radical complex and the corresponding species assigned to the
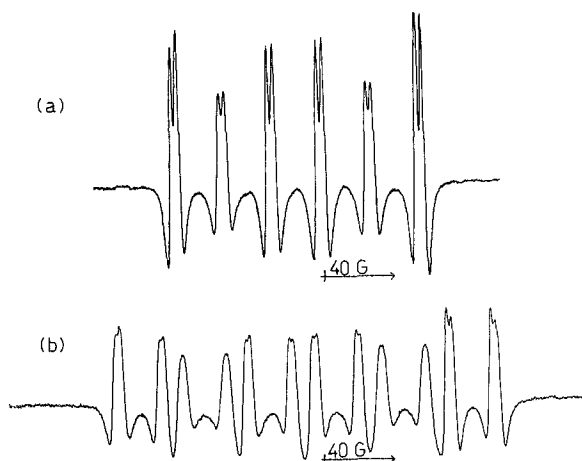

Fig. 1. The second-derivative ESR spectra in benzene at 25°C. (a) The parent DTBQ$\overset{.}{-}$Re$(CO)_4$ radical, (b) the substituted DTBQ$\overset{.}{-}$Re$(CO)_3$PPh$_3$ radical.

DTBQ$\overset{.}{-}$Re$(CO)_3$PPh$_3$ radical complex when PPh$_3$ was added to the solution. Preliminary experiments have shown that these organophosphine-substituted quinone—rhenium carbonyl radical complexes are thermally stable up to a few weeks in the dark. They can also be isolated by the HPLC/ESR technique and their other spectroscopic properties will be reported elsewhere.

With the enhanced resolution in the second-derivative presentation, the single proton hyperfine interaction which splits the six rhenium lines into doublets in the DTBQ$\overset{.}{-}$Re$(CO)_4$ radical clearly indicates that only one quinone is involved in the complex [9]. The thermal reaction when organophosphine is added leads to the rapid substitution of a "labile" CO group by the phosphine ligand:

$$\text{(structure)} \cdot Re(CO)_4 + PPh_3 \xrightarrow{\text{dark}} \text{(structure)} \cdot Re(CO)_3PPh_3 + CO \cdot \qquad (2)$$
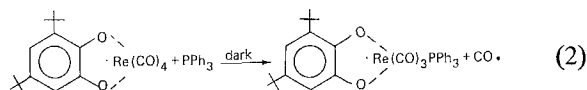
With triphenylphosphine only one CO group is exchanged as the ESR hyperfine structure (table 1) suggests the presence of one phosphorus nucleus. The substantial changes of the rhenium splitting between the parent radical complex and the phosphine-substituted radical, along with the noticeable variation in g factors indicate that there is significant redistribution of spin density. The trans effect in the substitution is consistent with this observation and thus suggesting that the exchange sites are at the equatorial positions. It is reasonable to expect that the distance between the Re and the P atom is larger than the Re and C bonds [10]. The apparently "small" splitting of the phosphorus is perhaps not too surprising. However, the significant increase of the rhenium splitting in the substituted complex strongly suggests a conjugative transfer of spin density when phosphine was added to replace a CO group.

While the reaction with bulky phosphines gave only monosubstitution, as apparently only one ligand molecule can be accommodated by the equatorial positions, organophosphines of smaller sizes such as trialkylphosphines and trialkylphosphites lead to disubstitution:
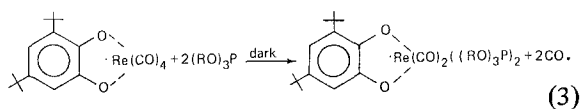
$$\text{(structure)} \cdot Re(CO)_4 + 2(RO)_3P \xrightarrow{\text{dark}} \text{(structure)} \cdot Re(CO)_2((RO)_3P)_2 + 2CO \cdot \qquad (3)$$

Table 1
ESR parameters of group VA organometal-substituted DTBQ$\dot{-}$Re(CO)$_4$ radical complexes in benzene solution

M	Radical complex	g factor	a_{Re} [a] (G)	a_M (G)
H	DTBQ$\dot{-}$Re(CO)$_4$	2.0032 ± 0.0002	28.2	(3.46)
P	DTBQ$\dot{-}$Re(CO)$_3$PPh$_3$	2.0012	38.0	24.7 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$P(C$_6$H$_4$CH$_3$)$_3$	2.0013	38.4	24.7 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$P(n-butyl)$_3$	2.0023	40.4	26.9 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$P(OPh)$_3$	2.0019	32.8	32.8 (1P)
	DTBQ$\dot{-}$Re(CO)$_2$(P(OCH$_3$)$_3$)$_2$	2.0009	49.9	30.8 (2P)
	DTBQ$\dot{-}$Re(CO)$_3$Ph$_2$PCH$_2$PPh$_2$	2.0010	38.7	27.04 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$Ph$_2$P(CH$_2$)$_2$PPh$_2$	2.0023	37.5	25.4 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$Ph$_2$P(CH$_2$)$_3$PPh$_2$	2.0016	37.9	26.3 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$Ph$_2$P(CH$_2$)$_4$PPh$_2$	2.0015	37.9	25.8 (1P)
As	DTBQ$\dot{-}$Re(CO)$_3$AsPh$_3$	2.0017	36	36 (1As)
^{121}Sb	DTBQ$\dot{-}$Re(CO)$_3$SbPh$_3$	2.0024	36	93 (57.25%)
^{123}Sb				50 (42.75%)
N	DTBQ$\dot{-}$Re(CO)$_3$N(C$_2$H$_5$)$_3$	2.0022	24.6	unresolved
P	DTBQ$\dot{-}$Re(CO)$_3$P(C$_6$H$_4$–N(CH$_3$)$_2$)$_3$	2.0015	38.0	24.7 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$Ph$_2$P(CH$_2$)$_2$AsPh$_2$	2.0016	37.5	25.1 (1P)
	DTBQ$\dot{-}$Re(CO)$_3$O=P(N(CH$_3$)$_2$)$_3$	2.0047	9.5 [b]	2.2 [b] (1P)

a) ^{185}Re(37.05%, $I = 5/2$) and ^{187}Re(62.93%, $I = 5/2$) could not be resolved as their magnetic moments differ only by 1%.
b) The small splitting of phosphorus along with the extremely small Re coupling constant indicate that the coordination site is the oxygen atom of the ligand.

The disubstituted radical complex, DTBQ$\dot{-}$Re(CO)$_2$ ((RO)$_3$P)$_2$, reveals hyperfine interactions with *two* equivalent phosphorus (fig. 2). Our tentative assignment again assumes that both phosphite ligands are replacing the two equatorial CO groups, consistent
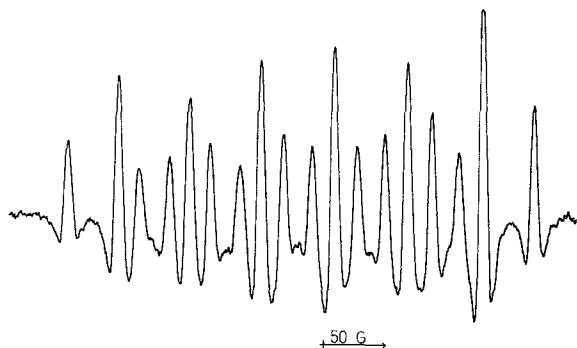

Fig. 2. The second-derivative ESR spectrum of the disubstituted DTBQ$\dot{-}$Re(CO)$_2$(P(O–CH$_3$)$_3$)$_2$ radical in benzene at 25°C.

with the observed small changes in the ESR parameters (table 1). Thermal disubstitution proceeded slowly enough at normal (room) temperature that it was possible to isolate the individual exchange step, indicating that the disubstitution takes place with one ligand at a time. When a bidentate phosphine such as Ph$_2$PCH$_2$CH$_2$PPh$_2$ was allowed to react with DTBQ$\dot{-}$Re(CO)$_4$, only monosubstitution occurred and the ESR spectrum showed only one resolved phosphorus splitting (table 1).

In the experimental spectra of these radical complexes (parent and substituted) the distances between the adjacent rhenium resonance lines are usually unequal. To obtain the average parameters, we have applied the second-order equation [11] in the form of

$$H_m = H_0 - am - (a^2/2H_0)[I(I + 1) - m^2], \qquad (4)$$

where H_m is the resonance field for the line with the nuclear spin quantum number m. Another "unusual" feature apparent in the spectra is the "symmetrical" broadening of the rhenium lines associated with

$m = 3/2$. This is much more difficult to rationalize and further studies including a model of the brownian tumbling of the microcrystallite [12] with a possible contribution from the second-order quadrupole effect in progress.

In addition to a number of organophosphine-substituted radicals reported in table 1, other group VA organometal ligands have also been studied in this rather unique exchange reaction. Triphenylarsine was found to undergo monosubstitution very slowly; the resultant $DTBQ^{\doteq}Re(CO)_3AsPh_3$ radical complex could be observed simultaneously with the parent radicals for a period of time before the substitution reaction was complete. The ESR parameters of this radical complex are reported in table 1. With triphenylantimony, the exchange reaction was so slow at room temperature that heat was required to produce the rhenium—antimony radical complex (table 1). On the other hand, triethylamine led to instant substitution as expected, but triphenylamine did not react with the parent $DTBQ^{\doteq}Re(CO)_4$ radical even at high temperatures. A possible explanation is the steric crowding by the phenyl groups at the nitrogen centre. Thus, by replacing two of the phenyl groups with H atoms, substitution reaction with aniline was found to proceed with ease. In the amine reactions no other radical ions such as the quinone radical anion have been observed.

Reactions with ligands containing either both nitrogen and phosphorus [such as $P(C_6H_4-N(CH_3)_2)_3$] or both phosphorus and arsenic, $Ph_2P(CH_2)_2AsPh_2$, the ESR observations of the substituted radical complexes indicates that the coordination site is the phosphorus. These preliminary results suggest that the order of the rate of the ligand exchange reactions in the $DTBQ^{\doteq}Re(CO)_4$ radical with group VA organometals is $N \approx P > As \gg Sb$. Griller and Ingold [13] have advanced the concept of persistence of carbon centered radicals which depends upon the environment. Here, in the thermally stable $DTBQ^{\doteq}Re(CO)_4$ organometallic radical complex we have further demonstrated the importance of a preferred "partnership".

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