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Preliminary communication

SYNTHESIS OF TETRAMETHYLAMMONIUM-*cis*-ACETYLPHENYLTETRACARBONYLRHENATE(I), A STABLE ACYCLIC ALKYLACYLMETAL COMPLEX

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Summary

Decarbonylation of $N(CH_3)_4^+$ *cis*-$(CO)_4Re(COCH_3)(COC_6H_5)^-$ (I) at 70°C gives a 97/3 mixture of $N(CH_3)_4^+$ *cis*-$(CO)_4Re(C_6H_5)(COCH_3)^-$ (II) and $N(CH_3)_4^+$ *cis*-$(CO)_4Re(CH_3)(COC_6H_5)^-$ (III) which equilibrate with one another at 40°C.

Recently the synthesis of $N(CH_3)_4^+$ *cis*-$(CO)_4Mn(COCH_3)(^{13}COC_6H_5)^-$ and its thermal decomposition to unlabelled acetophenone was reported [1, 2]. The thermolysis was proposed to proceed by CO loss and rearrangement to an unstable $N(CH_3)_4^+$ *cis*-$(CO)_4Mn(C_6H_5)(COCH_3)^-$ intermediate which underwent reductive elimination of acetophenone. We now report that decomposition of the corresponding rhenium compound, $N(CH_3)_4^+$ *cis*-$(CO)_4Re(COCH_3)(COC_6H_5)^-$ (I) gives $N(CH_3)_4^+$ *cis*-$(CO)_4Re(C_6H_5)(COCH_3)^-$ (II) as the major decomposition product. Similar alkylacyl-organometallics have been proposed as intermediates in the synthesis of ketones from $Na_2Fe(CO)_4$ and alkyl halides [3]. Several cyclic alkylacylmetal complexes [4] have been reported whose stability may be related to the reluctance of the compounds to give small ring ketones by reductive elimination. The unusual alkylacylzirconium compound, $(C_5H_5)_2ZrCH_3(COCH_3)$, in which the oxygen atom of the acyl unit is coordinated to zirconium, is stable to reductive elimination [5]. Chatt has reported difficulty in preparing and isolating $L_2MR(COR)$ compounds of Pt and Pd by carbonylation routes and was able to obtain only a single methylacetyl complex, $(Et_2PCH_2CH_2PEt_2)PtCH_3(COCH_3)$, in low yield [6].

Reaction of either $(CO)_5ReCOC_6H_5$ with CH_3Li or $(CO)_5ReCOCH_3$ with C_6H_5Li followed by treatment with $N(CH_3)_4^+Cl^-$ gave I as a yellow-orange crystalline solid, m.p. 133—134°C (dec), in 26 and 19% yields, respectively*. Thermolysis of I in acetone in a sealed NMR tube at 70°C for 2 h gave a 97/3 ratio of $N(CH_3)_4^+$ *cis*-$(CO)_4Re(C_6H_5)(COCH_3)^-$ (II), m.p. 135—137°C (dec), and $N(CH_3)_4^+$ *cis*-$(CO)_4$-

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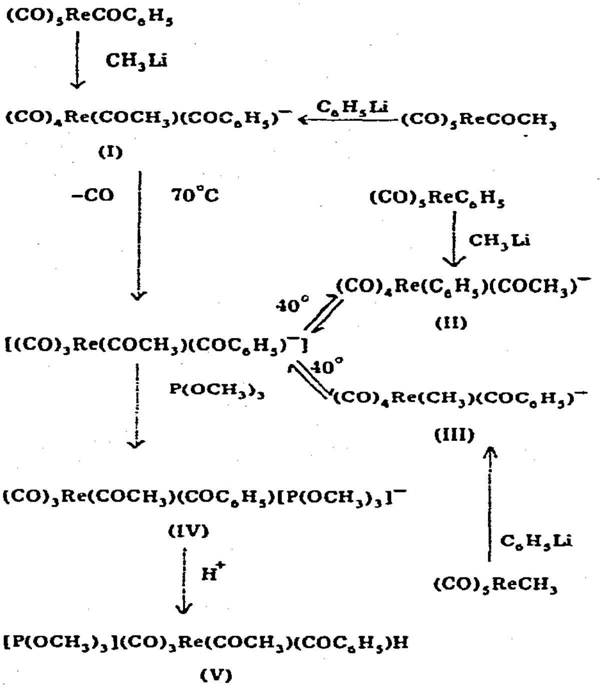
*Related protonated bis-acyl-rhenium compounds have been prepared [7].



$Re(CH_3)(COC_6H_5)^-$ (III), m.p. 131—132.5°C (dec). Further heating to 110°C for 3 h gave acetophenone. Compounds II and III were characterized by IR and NMR spectroscopy and by independent synthesis. Reaction of $(CO)_5ReC_6H_5$ with CH_3Li gave II in 53% yield whose NMR spectrum contains multiplets for *ortho* protons at δ 7.84 ppm and for *meta* and *para* protons at δ 6.80 ppm which are characteristic of $MC_6H_5^-$ units [8]. Reaction of $(CO)_5ReCH_3$ with C_6H_5Li gave III in 51% yield whose NMR spectrum contains a singlet at δ −0.38 ppm characteristic of a $ReCH_3$ compound.

Interconversion of II and III was found to be rapid under the conditions of their formation from decarbonylation of I. Either pure II or pure III rearranged to a 97/3 mixture of II/III (determined by ^1H NMR) upon heating to 40°C for several hours. The ratio of II/III therefore reflects the thermodynamic stability of the complexes and not the relative rates of migration from a $(CO)_3Re(COCH_3)(COC_6H_5)^-$ intermediate.

Decomposition of I at 70°C in the presence of $P(OCH_3)_3$ gave the phosphite substituted complex $N(CH_3)_4^+$ *fac*-$(CO)_3Re(COCH_3)(COC_6H_5)[P(OCH_3)_3]^-$ (IV) which was converted to *fac*-$[P(OCH_3)_3](CO)_3Re(COCH_3)(COC_6H_5)H$ (V) in 20% overall yield. Reaction of either II or III with $P(OCH_3)_3$ at 40°C also produced IV which was converted to V by protonation in 41 and 54% overall yield, respectively. We therefore propose that the formation of II and III from I, and the isomerization of II to III and of III to II, proceed through the same unsaturated tricarbonyl intermediate, $(CO)_3Re(COCH_3)(COC_6H_5)^-$.

IR, NMR, and analytical data

$N(CH_3)_4^+(CO)_4Re(COCH_3)(COC_6H_5)^-$ *(I)*. IR: ν(CO) 2063w, 1963s, 1943s, 1912s, ν(acyl) 1575, 1545 cm^{-1}. ^{1}H NMR: δ 7.46 (2H, m, *ortho* H's), 7.26 (3H, m, *meta* and *para* H's), 3.42 (12H, s, $N(CH_3)_4^+$), 2.26 ppm (3H, s, $COCH_3$). Anal. Found: C, 39.31; H, 3.99; N, 2.64. $C_{17}H_{20}NO_6Re$ calcd.: C, 39.23; H, 3.87; N, 2.69%.

Compound I was further characterized by conversion [7] to the protonated species $(CO)_4Re(COCH_3)(COC_6H_5)H$, m.p. 82—83°C; a 60% overall yield from $(CO)_5ReCOC_6H_5$ and CH_3Li was obtained. IR: 3400 (br), ν(CO) 2088m, 1996vs, 1960s cm^{-1}. ^{1}H NMR: δ 7.45—7.80 (5H, m, C_6H_5), 2.91 (3H, s, CH_3), 17.5 ppm (1H, broad s, enol H). Mass spectrum (*m/e*, %) 433(25), 431(15), 377(11), 327(11) 321(11), 293(11), 271(10), 122(11), 106(80), 105(100), 78(59), 77(91). Exact mass: 447.9950 ($C_{13}H_9O_6Re$ calcd.: 447.9959).

$N(CH_3)_4^+(CO)_4Re(C_6H_5)(COCH_3)^-$ *(II)*. IR: ν(CO) 2059w, 1950s, 1943s, 1900s cm^{-1}. ^{1}H NMR: δ 7.84 (2H, m, *ortho* H's), 6.80 (3H, m, *meta* and *para* H's), 3.38 (12H, s, $N(CH_3)_4^+$), 2.26 ppm (3H, s, $COCH_3$). Anal. Found: C, 38.96; H, 4.35; N, 2.83. $C_{16}H_{20}NO_5Re$ calcd.: C, 39.02; H, 4.09; N, 2.84%.

$N(CH_3)_4^+(CO)_4Re(CH_3)(COC_6H_5)^-$ *(III)*. IR: ν(CO) 2048w, 1943s, 1888m cm^{-1}. ^{1}H NMR: δ 7.50 (2H, m, *ortho* H's), 7.28 (3H, m, *meta* and *para* H's), 3.38 (12H, s, $N(CH_3)_4^+$), –0.38 (3H, s, CH_3)*.

$N(CH_3)_4^+(CO)_3Re(COCH_3)(COC_6H_5)[P(OCH_3)_3]^-$ *(IV)*. ^{1}H NMR: δ 7.58 (2H, m, *ortho* H's), 7.26 (3H, m, *meta* and *para* H's), 3.56 (9H, d, *J* 11 Hz, $P(OCH_3)_3$), 3.38 (12H, s, $N(CH_3)_4^+$), 2.26 ppm (3H, s, $COCH_3$).

$[P(OCH_3)_3](CO)_3Re(COCH_3)(COC_6H_5)H$. Compound IV was further characterized by conversion [7] to the protonated species *fac*-$[P(OCH_3)_3](CO)_3Re(COCH_3)\cdot(COC_6H_5)H$ (V), m.p. 89—90°C. IR: ν(CO) 2031s, 1957s, 1925s cm^{-1}. ^{1}H NMR: δ 7.65 (2H, m, *ortho* H's), 7.45 (3H, m, *meta* and *para* H's), 3.48 (9H, d, *J* 11 Hz, $P(OCH_3)_3$), 2.88 (3H, s, CH_3), 22.30 ppm (1H (br) s, enol H). Anal. Found: C, 33.36; H, 3.26; P, 5.56; Re, 34.08. $C_{15}H_{18}O_8PRe$ calcd.: C, 33.15; H, 3.34; P, 5.70; Re, 34.26%.

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*No analysis due to instability.